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SYNTHESIS OF HIGH-ENERGY 1,2,3,4-TETRAZINE 1,3-DI-N-OXIDES
ANDPENTAZINE POLY-N-OXIDES

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13. ABSTRACT (Maximum 200 words)

At the Contemporary Energetics Conference at The MITRE Corporation, McLean, VA on July 20, 2003. In this talk I summarized our DARPA/AFOSR and published Russian efforts to prepare DTTO, IsoDTTO and other energetics. In the present set of overheads I have added further routes (overheads 35, 43, 46 and 50-59) to be investigated for synthesis of various 1,2,3,4-tetrazine, 1,3-di-N-oxides, DTTO, and IsoDTTO. Synthesis of triazolotetrazine dioxides (overhead 35) is now being emphasized. There are notes and explanations on almost all of the overheads to make them more understandable. Such additions were suggested at our June meeting, 2004. I believe that the additions make our work and my talk much more intelligible. In the present overheads our studies of synthesis of 1-nitroacetylenes and dinitroacetylene as sponsored by DARPA/AFOSR have not been included.

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17. SECURITY CLASSIFICATION
OF REPORT18. SECURITY CLASSIFICATION
OF THIS PAGE19. SECURITY CLASSIFICATION
OF ABSTRACT

20. LIMITATION OF ABSTRACT

Synthesis of 1,2,3,4-Tetrazines, 1,2,3,4-Tetrazine Di-N-oxides, Pentazole Derivatives, Pentazine Poly-N-oxides, and Nitroacetylenes

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M. Venugopal, D. Srinivasulu, and H. Shechter

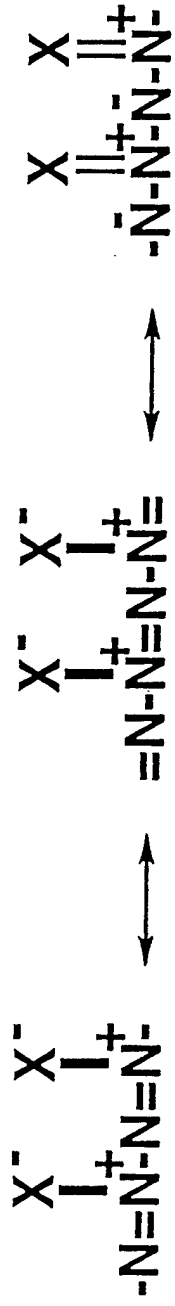
Department of Chemistry, The Ohio State University
Columbus, Ohio

This presentation will be primarily a review of research on the chemistry of 1,2,3,4-tetrazines and 1,2,3,4-tetrazine di-N-oxides as published from Moscow since 1988 by many chemists in the Zelinsky Institute and as explored by Dr. Venugopal at OSU since early 2001. In this talk many new and interesting structures will be considered and if time permits, many approaches to synthesis of energetic molecules will be proposed.

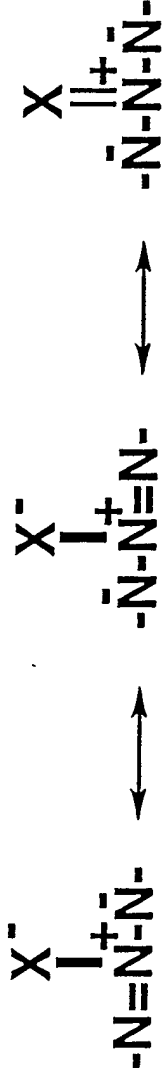
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Stabilized Systems

Alternate Positive-Negative Charges (APNC)



This is truly an important concept in considering new synthesis of high-energy materials!



Substitute N for O
in nitrate (NO_3^-),
nitrite (NO_2^-), pernitrate
($\text{O}=\text{O}-\text{NO}_2$) and related
oxygen-nitrogen compounds!
($\text{R}-\text{NO}_2$, $\text{R}-\text{ONO}$, $\text{R}-\text{ONO}_2$, etc.)

$\text{X} = \text{O}, \text{NR}, \text{ and } \text{CR}_2$

This concept should be made clear to every student of Beginning Chemistry.

This concept should be extended to boron and phosphorus compounds!

Menkin, 1988; Churakov, 1991

The concept of APNC was originated by Menkin, a chemist in Russia, and serves as the basis for my presentation today. The ideas will be extended to many new energetic molecules as yet unknown.

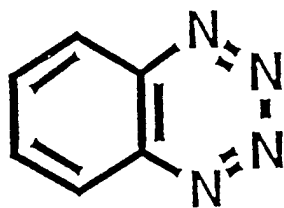
Stabilized N-Oxides



unstable

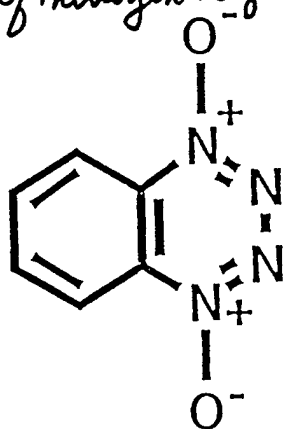
Many chemists in the 1940s tried to prepare N_6 , a benzene analog.

This molecule has not been generated seriously at low temperatures. Is it stable? Can it be isolated and used?



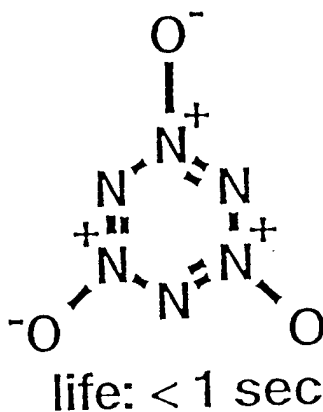
unstable

This molecule undergoes loss of nitrogen to give benzene!



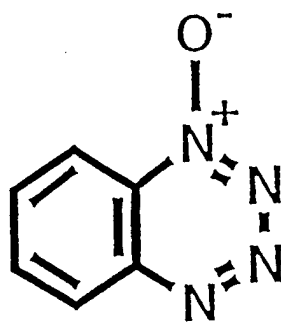
unstable

This tetrazine dioxide loses N_2 to form o-dinitrobenzene. No one has examined this molecule at low temperatures.



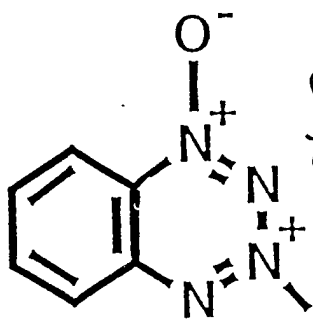
life: < 1 sec

very few chemists know that this molecule, N_3O_3 , will go through a mass spectrometer. This molecule is a trimer of nitrous oxide, N_2O .



preparable

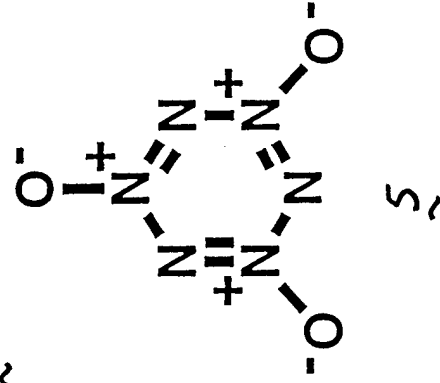
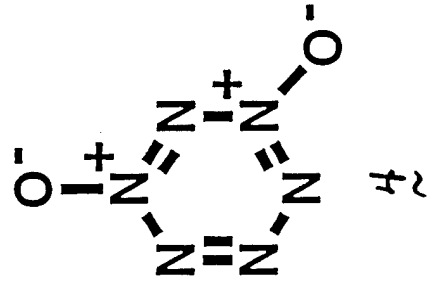
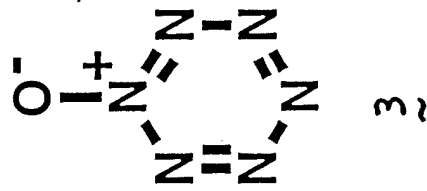
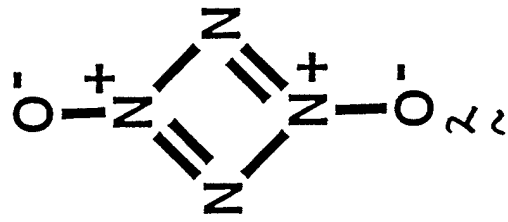
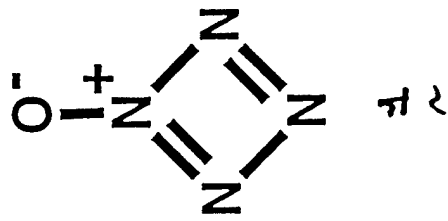
This tetrazine N-oxide melts at $72-74^\circ C$ and can be "kept" for 6-7 hours before decomposition.



stable, usable

This molecule is stable, now readily prepared, and melts at $172-174^\circ C$.

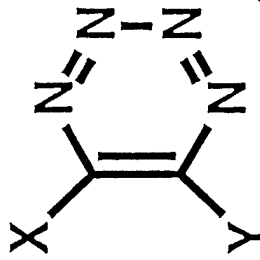
The Zelinski chemists have been studying this molecule since the early 1990s or even earlier. Well over 30 Russian have been studying this molecule!



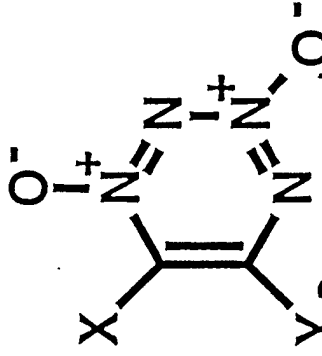
Bartlett et al, J. Phys. Chem., 2001

Prof. Bartlett visited OSU and was informed of the APNC concept. He and his colleagues have calculated that 2 is more stable than 1 and 5 is more stable than 3 and 4. As yet 2 has not been prepared.

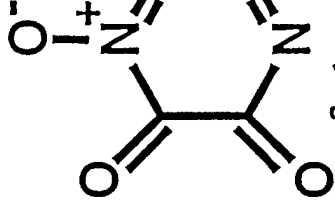
Synthesis of High-Energy Heterocycles



We at OSA are studying preparation, stability, and utility of 1,3,4-tetrazines at low temperatures. If such tetrazines can be utilized, this whole area will become very important and economical.

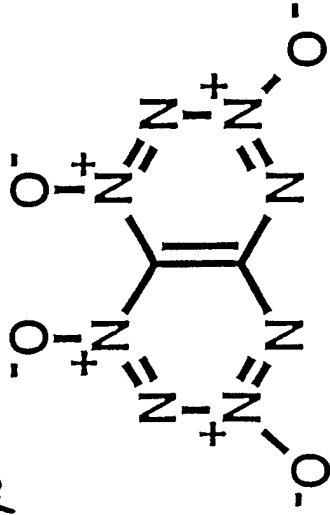


This is a major objective of the program at OSA. Very important.

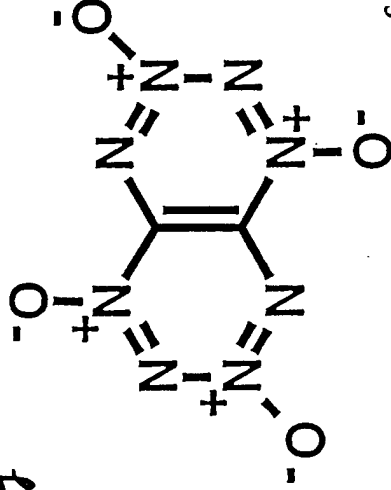


A very important molecule whose synthesis is being studied at OSA. This molecule should be an excellent source of N_2O for use in synthesis of this molecule at OSA on our engines and combustion modeler.

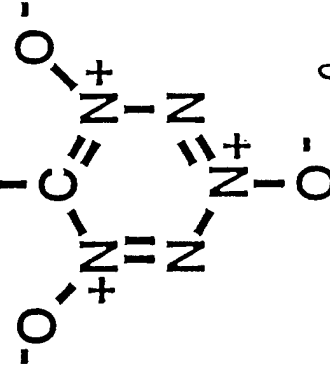
We are beginning study of synthesis of this molecule at OSA on our engines and combustion modeler.



DTTO: An enormously important molecule. Synthesis of DTTO is the major objective of the OSA- DARPA- Air Research effort. This molecule is truly important! The Russians are paying secret!!!



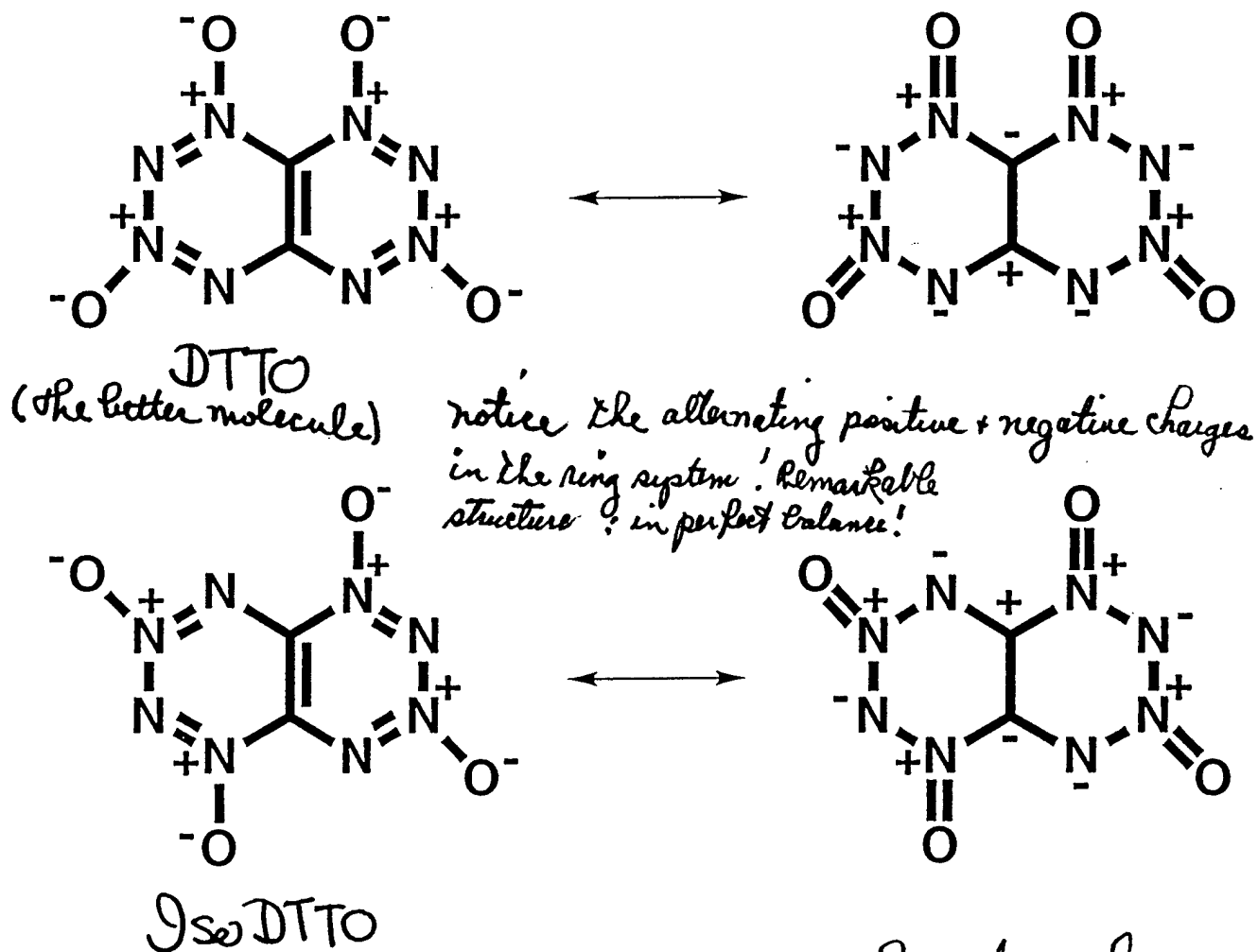
DTTO: an enormously important molecule also being studied in Russia. A major objective of the program by DARPA/Air Force at OSA. See calculations in a later slide.



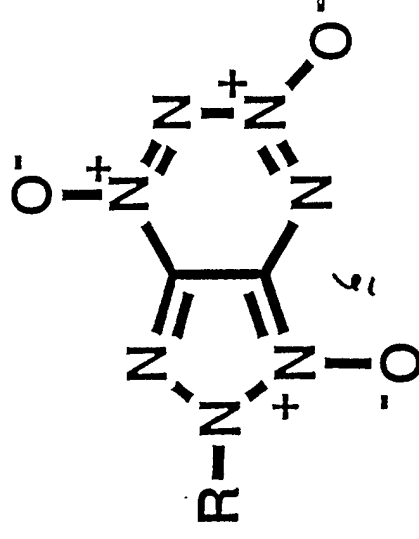
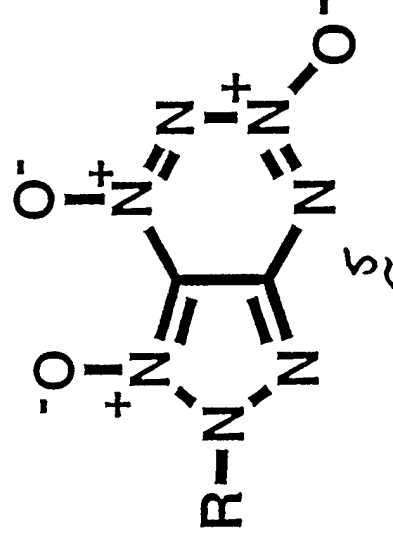
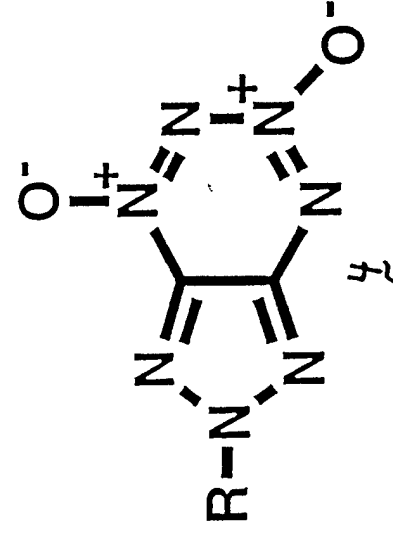
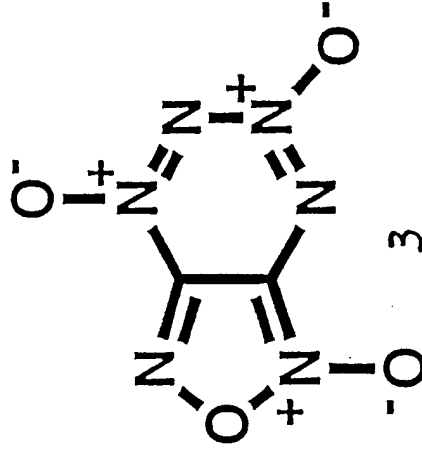
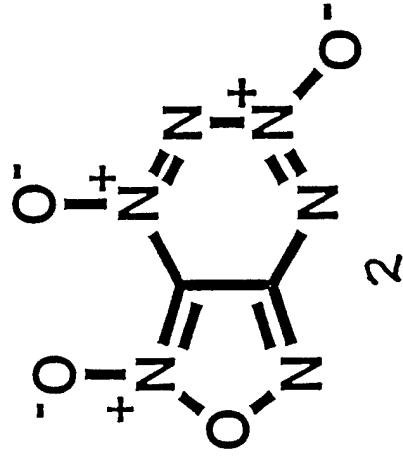
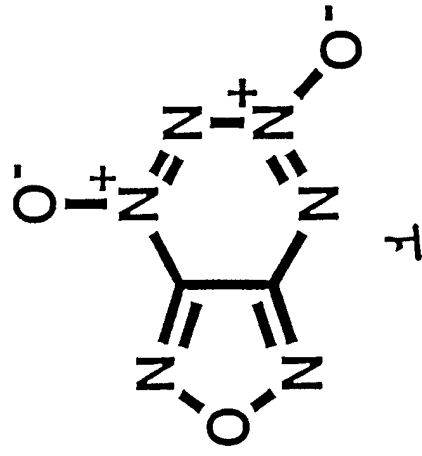
Calculations are in progress.

This is an unknown molecule at present. We wish to study its synthesis at OSA. Additional funding will be necessary if study of this molecule is to be emphasized.

The research of Dr. Venugopal at OSA is totally dedicated to practical synthesis of DTTO or/and IsoDTTO. This project needs additional funding if Dr. Venugopal is to stay at OSA and complete this effort

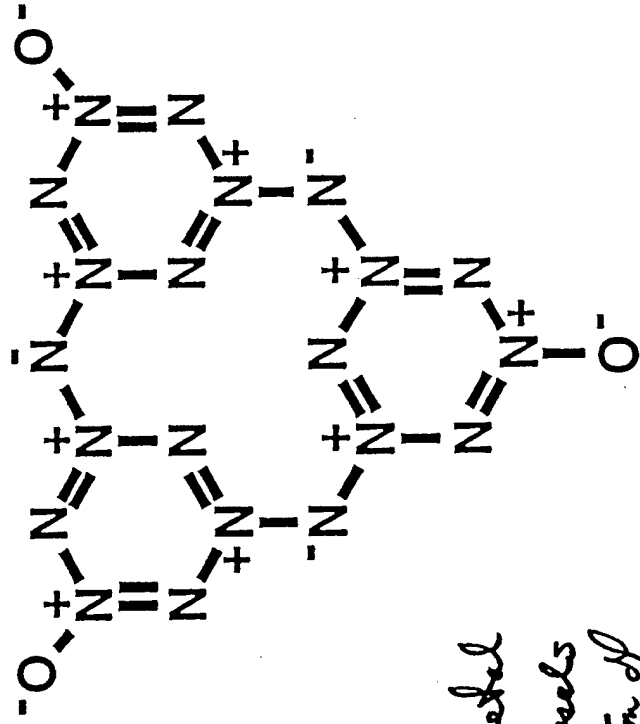
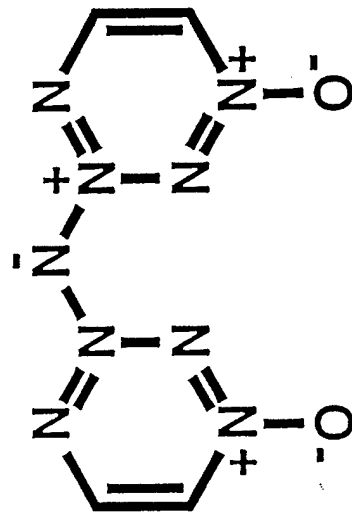
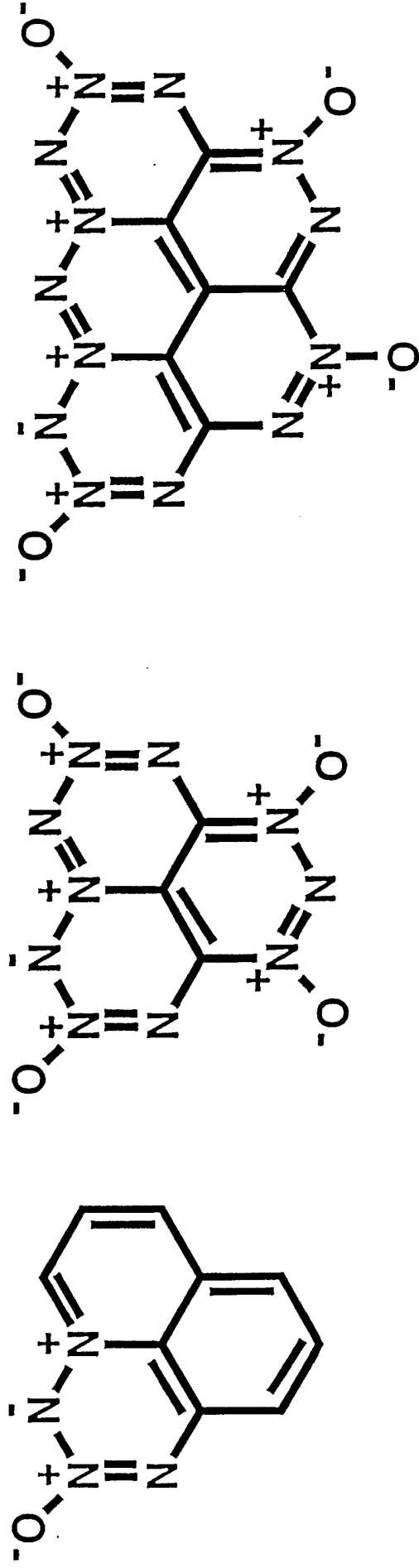


This slide illustrates the APNC characters of DTTO and IsoDTTO. The alternating positive and negative charges in the ring systems are illustrated. Tartakowski emphasized this concept in his West Coast seminar in 1995. We should learn where the Russians and the Chinese are in syntheses of DTTO and IsoDTTO. Are these molecules going to be practical?



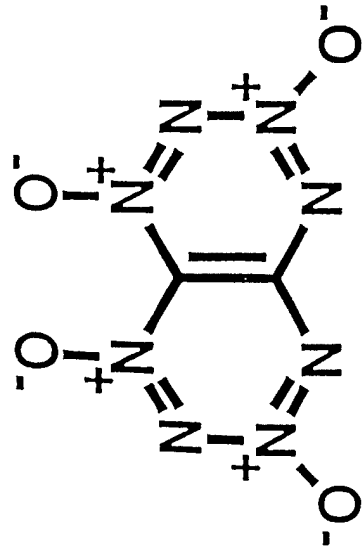
Compound 1 has been synthesized in Moscow and at OSL. It is hoped to convert 1 to 2 and 3. As yet this effort has not been successful. Compounds 2 and 3 are isomers of DTT and DDT. At present we do not have good crystals of 1. We want an X-ray analysis of 1 (ferrous tetrazine 1,3-di-N-oxide). Identifying the structures of the hydrolysis products of 1 will take time. Study has been initiated of synthesis of 4. This study needs further funding.

Alternating Positive-Negative Heterocycles



(N₂₁O₃³⁺)

These molecules have been theorized by Henkin et al to be stable! These molecules lead to proposals of study of polymerization and copolymerization of N₂O and oxides (2N₂). Scientists should really study fixation of N₂O as 2N₂! Later slides need amphoteric studies!

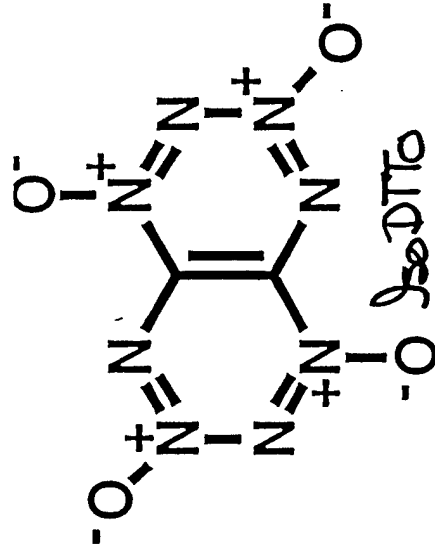


DTTO

$$\rho = 2.419 \text{ g cm}^{-3}$$

$$\Delta H_f = 179.5 \text{ kcal mol}^{-1}$$

$$P_{CJ} = 131.4 \text{ GPa}$$

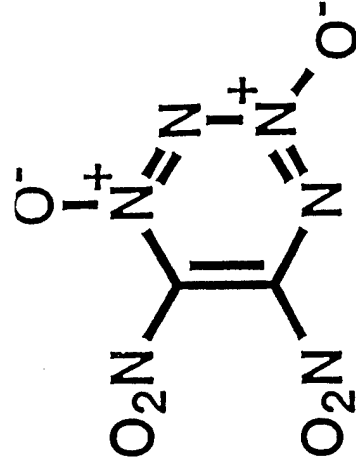


-O IsoDTTO

$$\rho = 2.484 \text{ g cm}^{-3}$$

$$\Delta H_f = 175.7 \text{ kcal mol}^{-1}$$

$$P_{CJ} = 131.8 \text{ GPa}$$



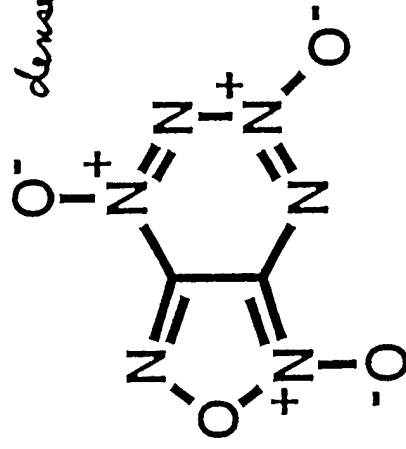
Is such a monocyclic compound stable or practical?

$$\rho = 2.072 \text{ g cm}^{-3}$$

$$\Delta H_f = 134.3 \text{ kcal mol}^{-1}$$

$$P_{CJ} = 50.6 \text{ GPa}$$

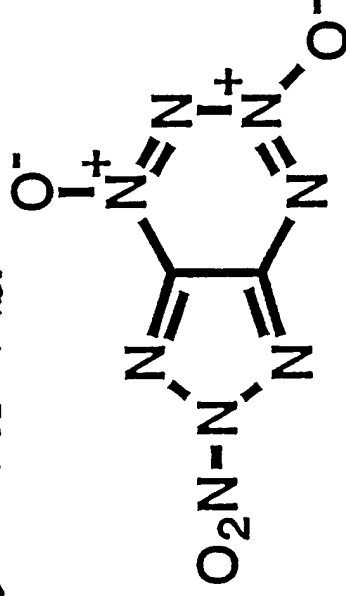
will these molecules be this dense?



$$\rho = 2.191 \text{ g cm}^{-3}$$

$$\Delta H_f = 128.6 \text{ kcal mol}^{-1}$$

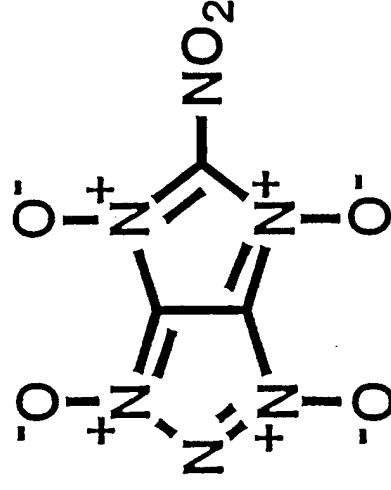
$$P_{CJ} = 61.8 \text{ GPa}$$



$$\rho = 2.179 \text{ g cm}^{-3}$$

$$\Delta H_f = 158.1 \text{ kcal mol}^{-1}$$

$$P_{CJ} = 61.96 \text{ GPa}$$



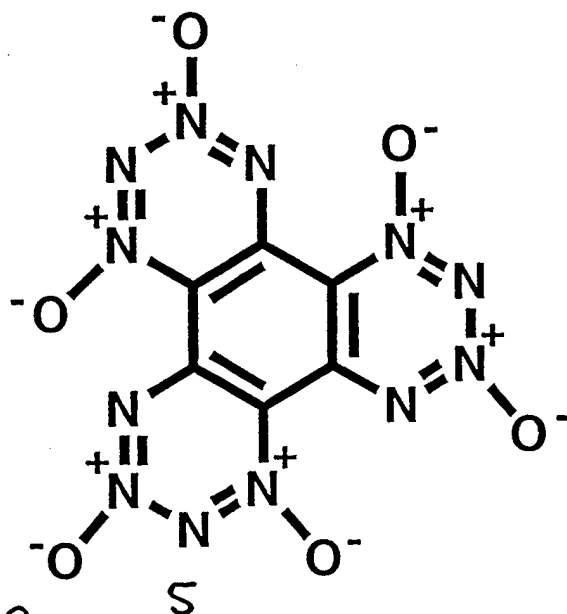
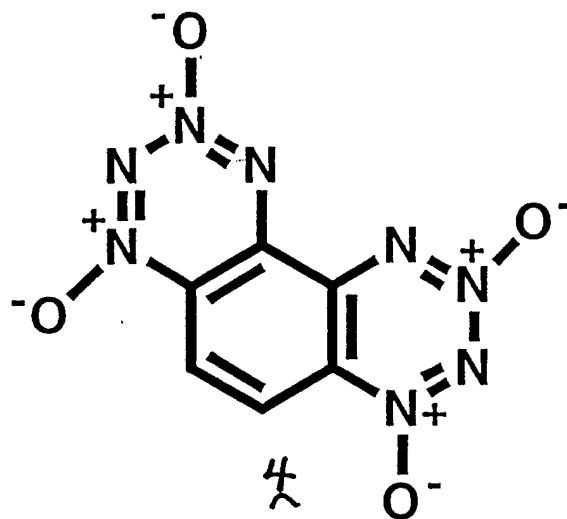
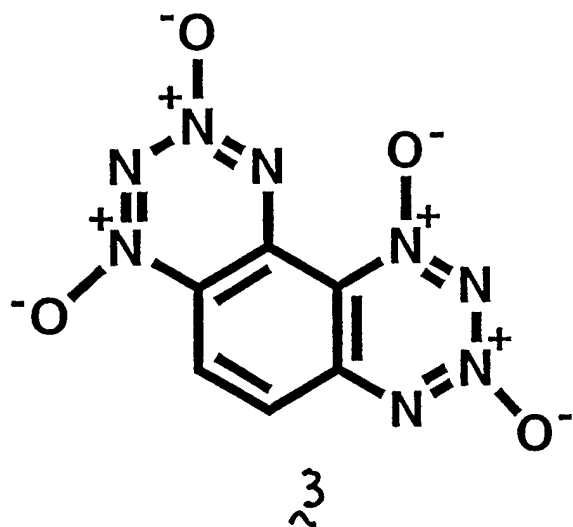
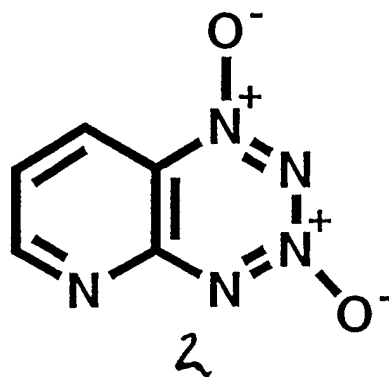
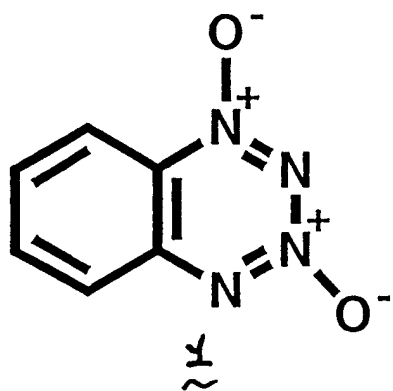
$$\rho = 2.191 \text{ g cm}^{-3}$$

$$\Delta H_f = 128.6 \text{ kcal mol}^{-1}$$

$$P_{CJ} = 61.8 \text{ GPa}$$

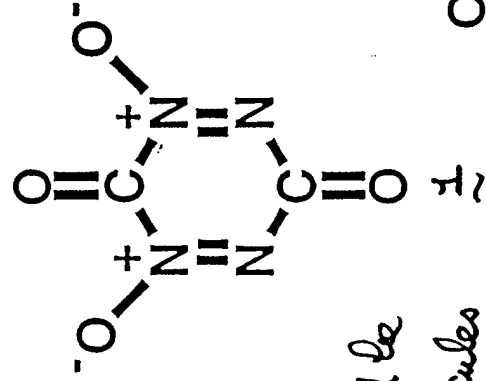
These calculations were made by H. Ammon at the Univ. of Maryland. DTTO and IsoDTTO are spectacular!

DTTO and IsoDTTO

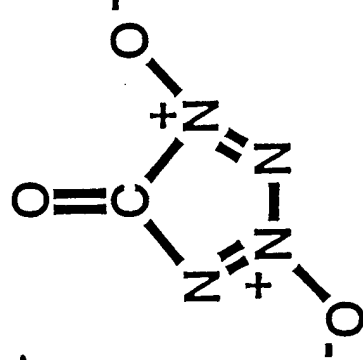
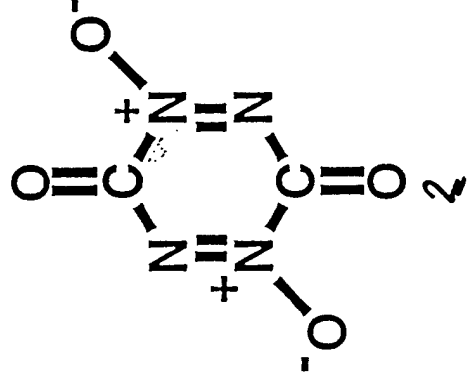


Compounds 1, 2, and 3 have been synthesized in Moscow. They are quite stable. We are sure that preparation of 5 is being attempted by Zelinsky chemists.

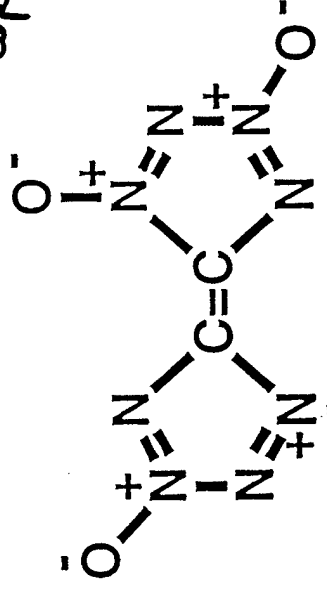
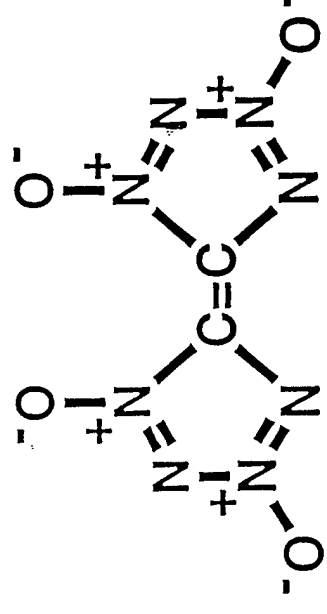
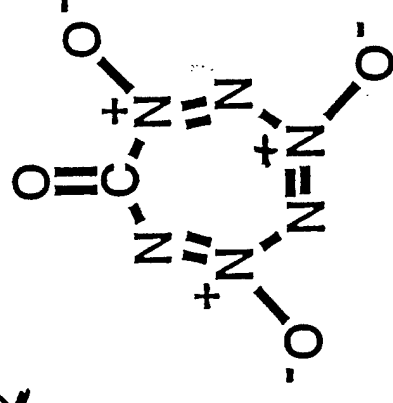
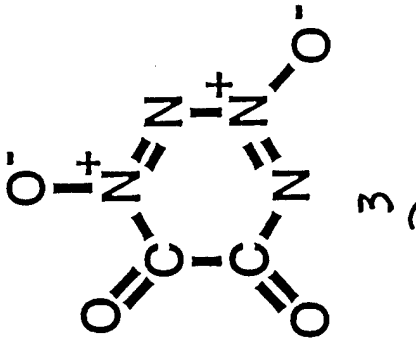
Carbon Monoxide-Nitrous Oxide Heterocycles



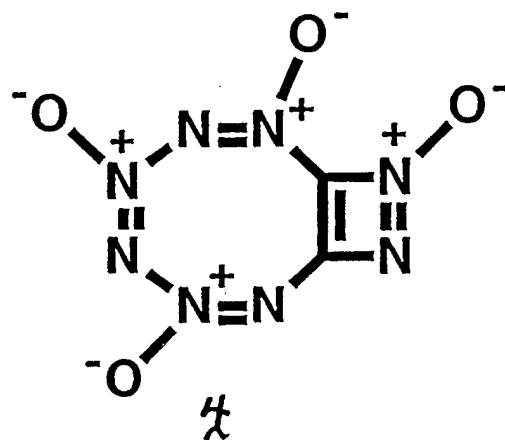
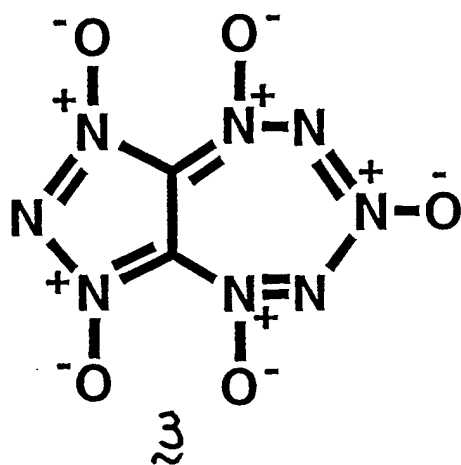
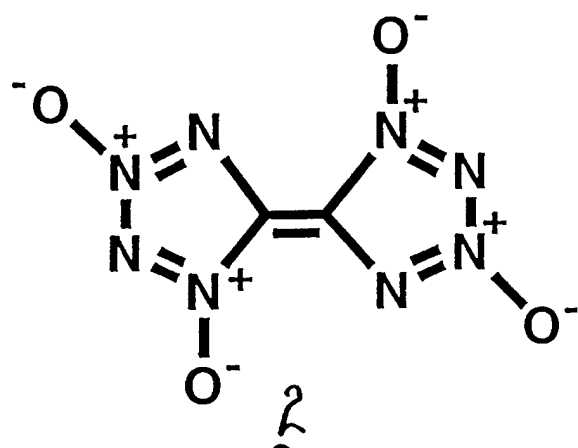
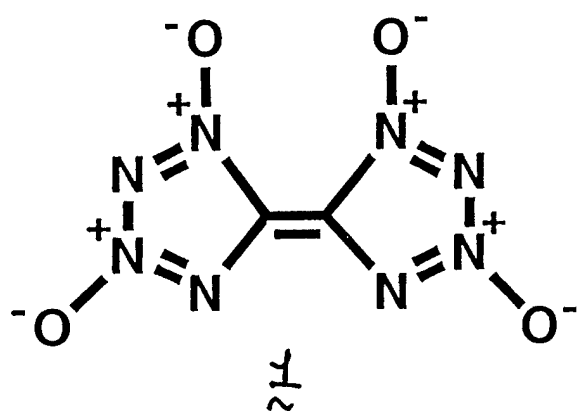
1 and 2 should be
practical molecules
preparable from
phosgene, $[\text{COCl}_2]$ and
hydroxylamine or phosgene
and NaNO_2 !!
important ideas!



Syntheses of 1-3
should be made
major efforts!!
These molecules also
lead to study of the
chemistry of NPO , PNO ,
 ONO , and NBO !! These ideas
will be developed further at ASA.



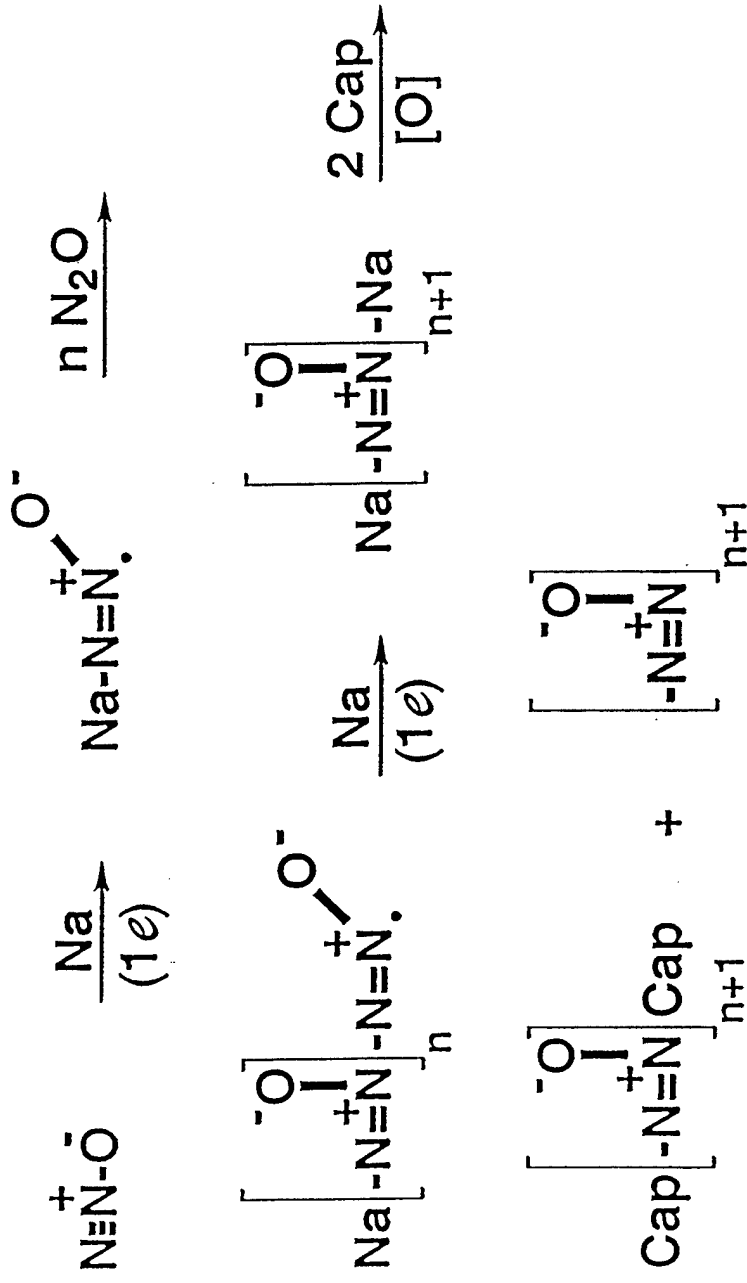
These are all new compounds being proposed by ASA for study. They
are in perfect C_2 and N_2 balance -- and may be valuable as gasoline additives.



Compounds 1 and 2 are E + Z-isomers. Compounds 3 + 4 are also attractive. The theory and calculations of the molecules on slides 10 and 11 are to be developed.

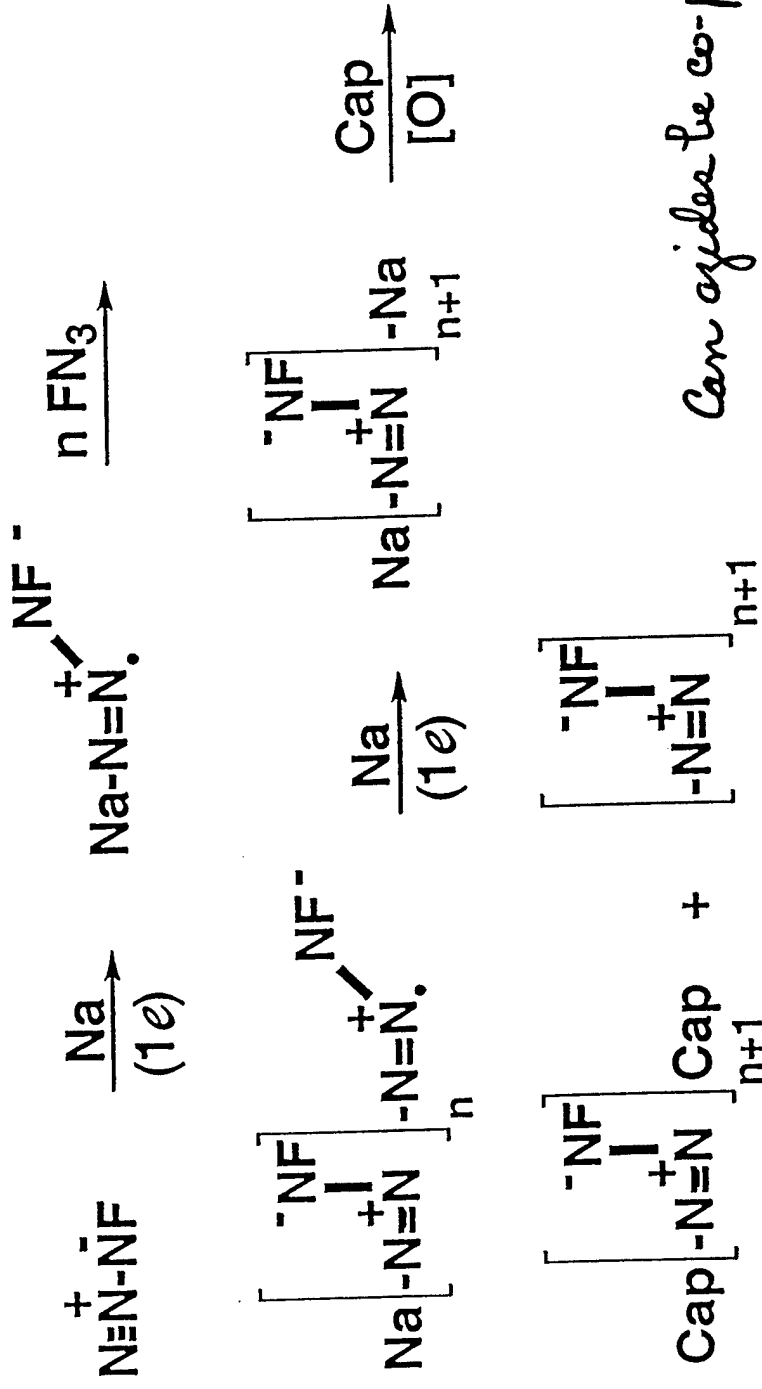
HS

Polymerization of Nitrous Oxide

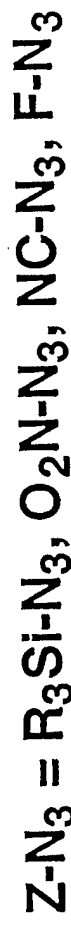


Can N_2O and/or azides be polymerized or copolymerized?
 Can N_2O undergo cyclodimerization or cyclopolymerization?
 N_2O adds to acetylenes to give α -dioxolides. Can N_2O and acetylenes be copolymerized?

Polymerization of Azides

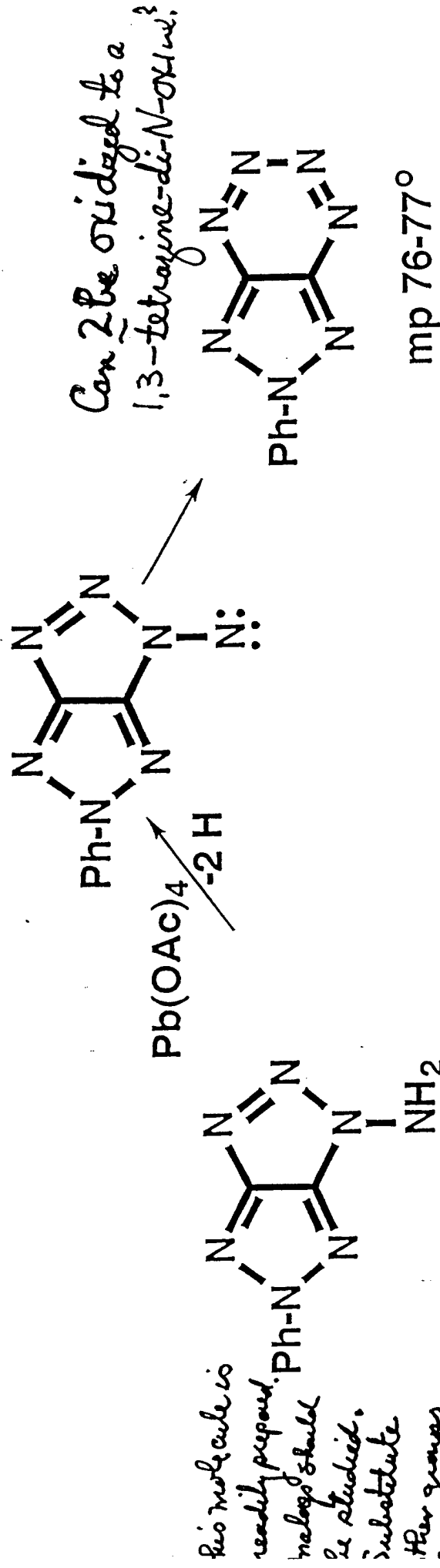


Can azides be co-polymerized?



This will be of great significance if accomplishable. Such programs should be initiated. Active metals add to N_2O !!

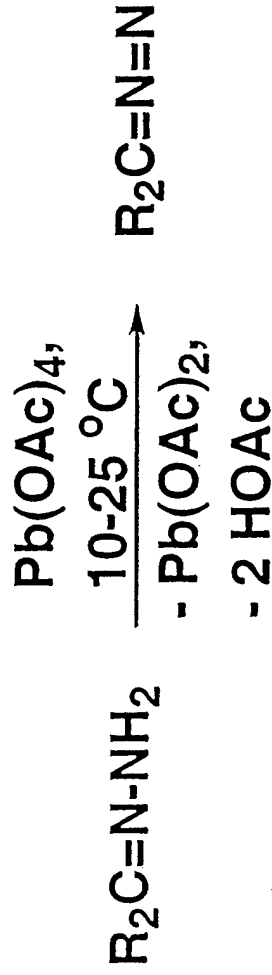
Stable [1,2,3]-Triazolo[1,2,3,4]tetrazines



Triazolotetrazine 2 is preparable and fairly stable. It is the only known stable 1,2,3,4-tetrazine and its chemistry should be determined. Tetrazine 2 can not ring-open to a bis-di-oxo compound. The oxidation and derivatization of 2 should be studied. The phenyl group in 2 should be replaced by a removable group!

Ohsawa, Chem. Comm., 1988

Oxidation of Hydrazones with $\text{Pb}(\text{OAc})_4$



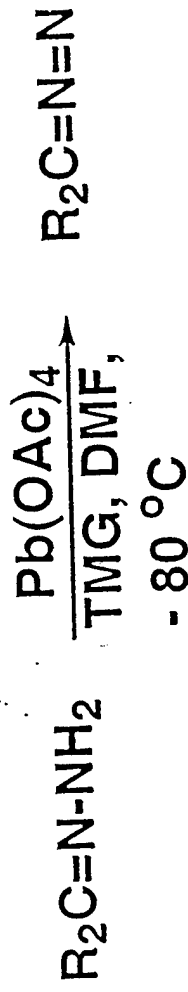
Stabilizing groups are highly electronegative and conjugating: RO_2C , $\text{C}=\text{C}$, $\text{N}=\text{C}$, Ar, etc.



the acetic acid diazo compounds unless they are highly stabilized (acid resistant).

Monohydrazones are rapidly oxidized to monodiazocompounds by lead tetraacetate. Unless the diazocompounds are stabilized by conjugating groups, they are decomposed very rapidly by the acetic acid produced. This method is not useful for synthesis of typical diazo compounds. Of interest is development of methodology in which the diazo compounds are not destroyed by acetic acid and elevated temperatures.

Oxidation of Hydrazones with $\text{Pb}(\text{OAc})_4$ in Tetramethylguanidine/Dimethylformamide



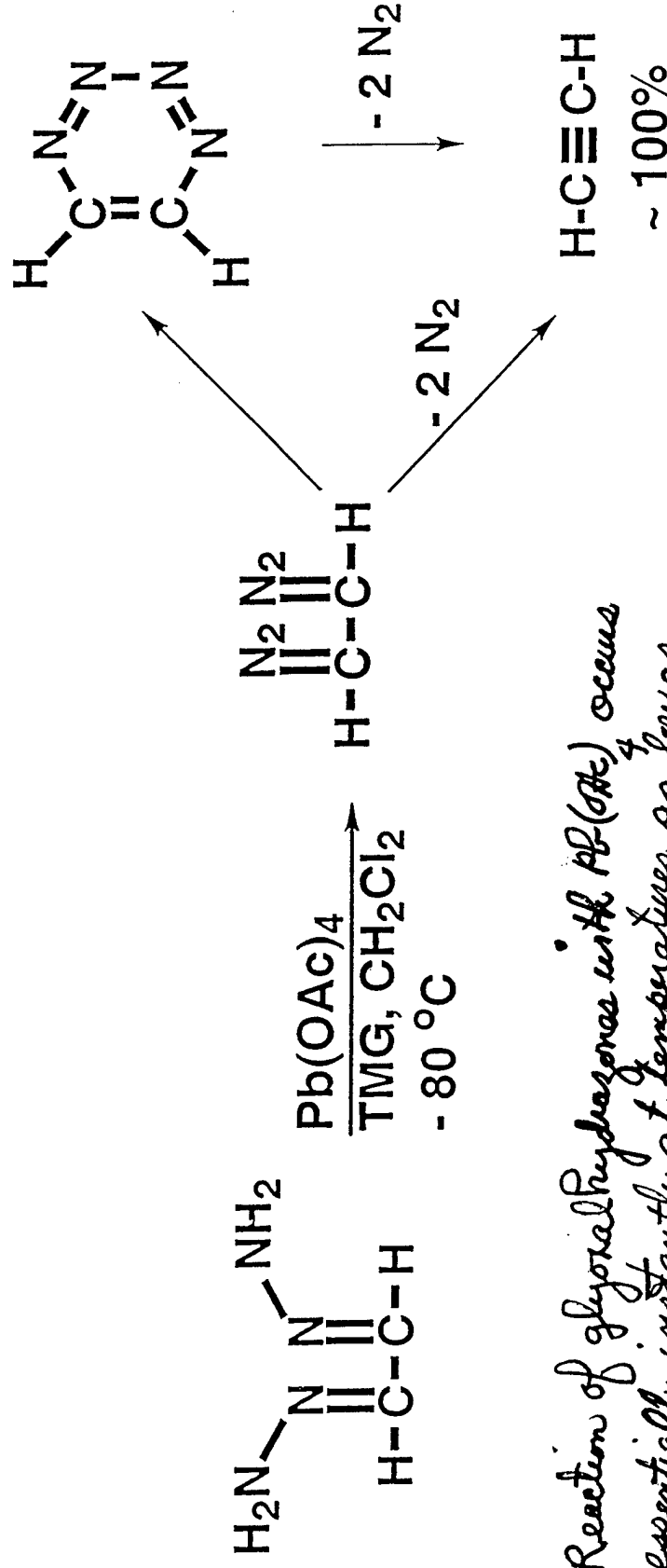
Excellent General Method; J. Org. Chem., 1995

This method is the best known method for preparing monodiaz compounds at low temperatures. This method was originated and developed at Ohio State and published in 1995 as indicated. Of present interest and as sponsored by DARPA/AIR FORCE is extension of the method to vicinal-dihydrazones for practical syntheses of usable 1,2,3,4-tetraazines.

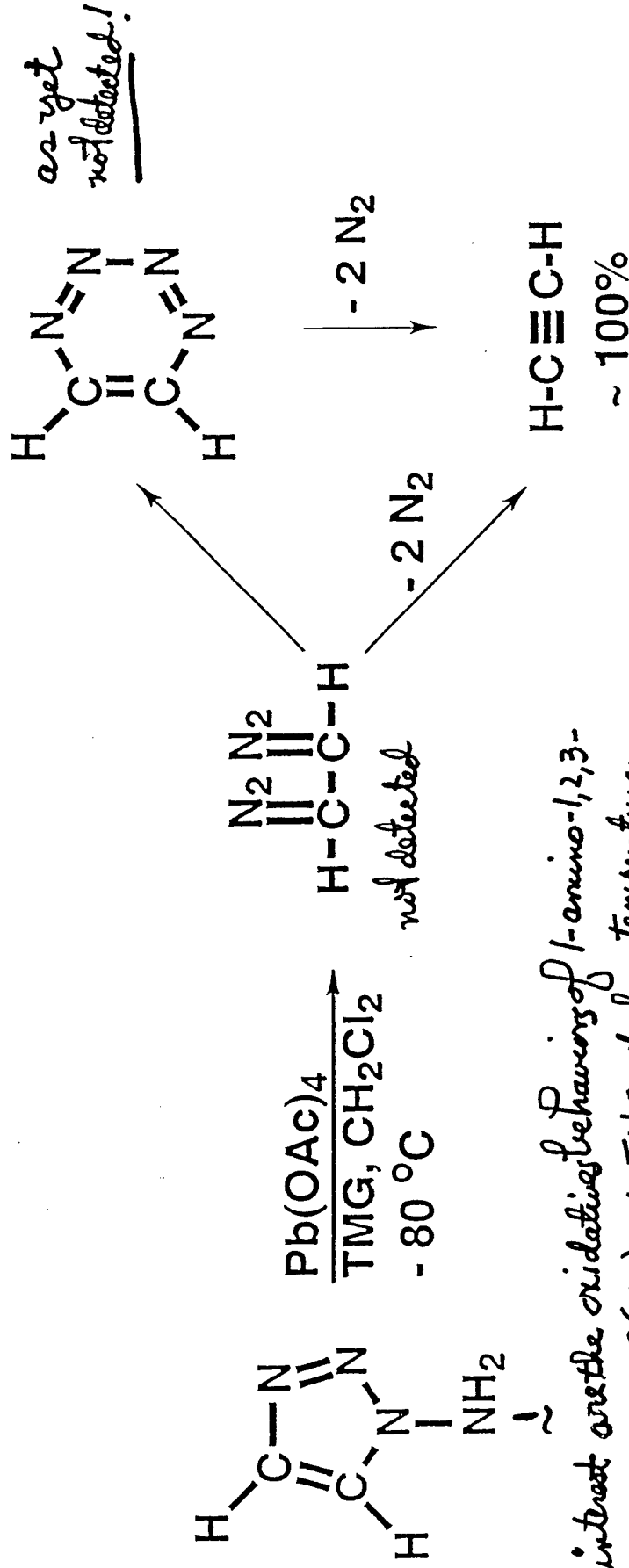
The TMG neutralizes the acetic acid and protects every diazo compound as yet prepared. Is the

method usable for practical syntheses of vicinal bis-diazo compounds? The DMF serves as an excellent solvent for above reaction mixtures at low temperatures. The diazo compounds have been kept for days at -78°C .

Glyoxal Dihydrazones, Pb(OAc)₄, TMG, and CH₂Cl₂



Reaction of glyoxal hydrazones with H_2SO_4 occurs essentially instantly at temperatures as low as -120°C to give acetylene essentially quantitatively. It is not known if 1,2,3,4-tetraene is actually produced in these experiments. There are problems in these very low temperature oxidations in that the reagents are not very soluble, the oxidations should be tried in liquid CO_2 at low temperatures. Vanadium oxidants should be investigated.



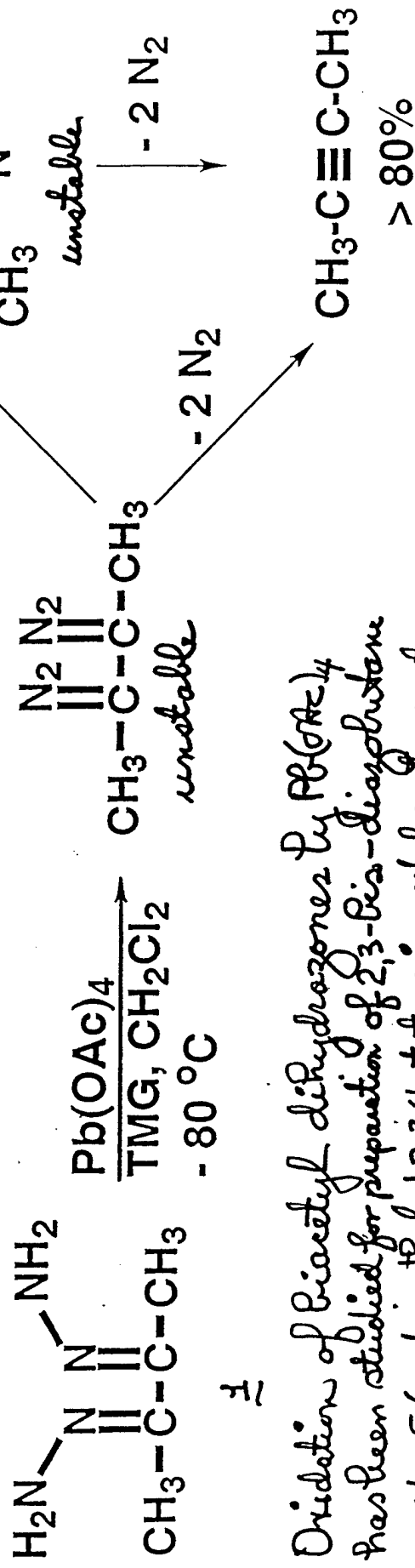
of interest are the oxidative behaviors of 1-amino-1,2,3-triazole with $\text{Pb}(\text{OAc})_4$ in TMG at low temperatures.

What is the behavior of 1-nitro-1,2,3-triazole (1)

what is found "1" is that 1 decomposes with loss of 2 N_2 at $< -88^\circ\text{C}$. The behavior above is identical with 1,2,3,4-tetrazine in slide 19.

that for glyoxal N: dihydrozone is unstable at $< -88^\circ\text{C}$ and decompose or 1,2-bis-diagoothane are rapidly to yield acetylene (~100%). determine reaction mechanism.

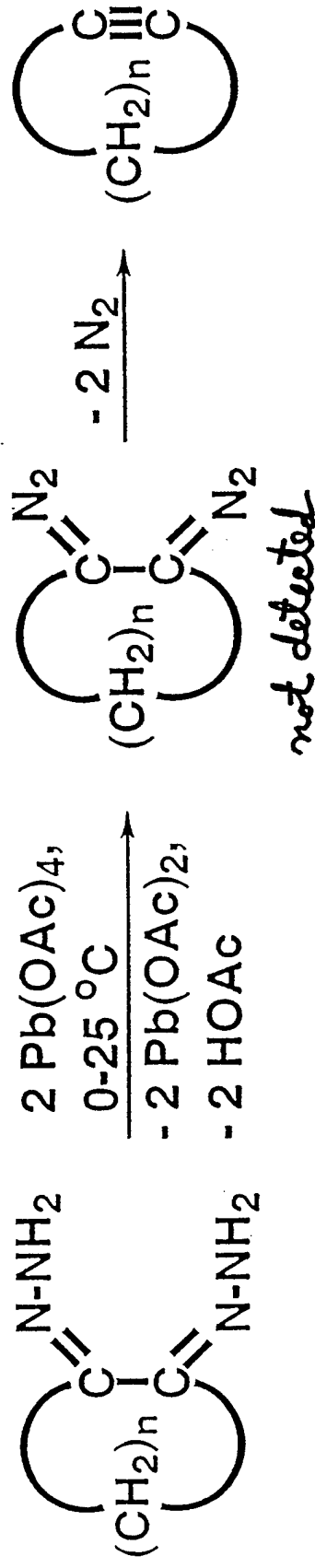
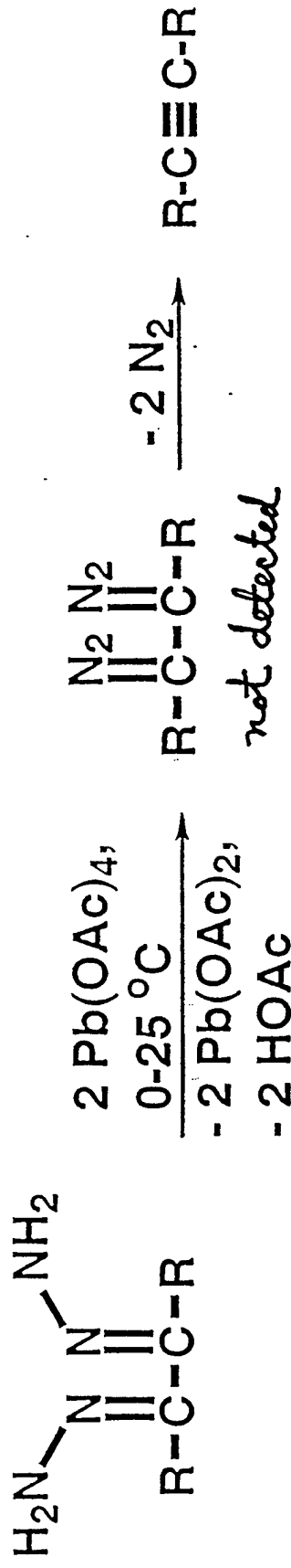
Biacetyl Dihydrazones, $\text{Pb}(\text{OAc})_4$, TMG, and CH_2Cl_2



Oxidation of biacetyl dihydrazones by $\text{Pb}(\text{OAc})_4$ has been studied for preparation of 2,3-bis-diazobutane and for 5,6-dimethyl-1,2,3,4-tetrazine at low temperatures.

In all present experiments oxidation of I produces 2-butyne in $> 80\%$ yield essentially instantly (on adding the $\text{Pb}(\text{OAc})_4$). The structures of the actual intermediates in the above experiments are as yet unknown!

Oxidation of Vic-Dihydrazones with $\text{Pb}(\text{OAc})_4$

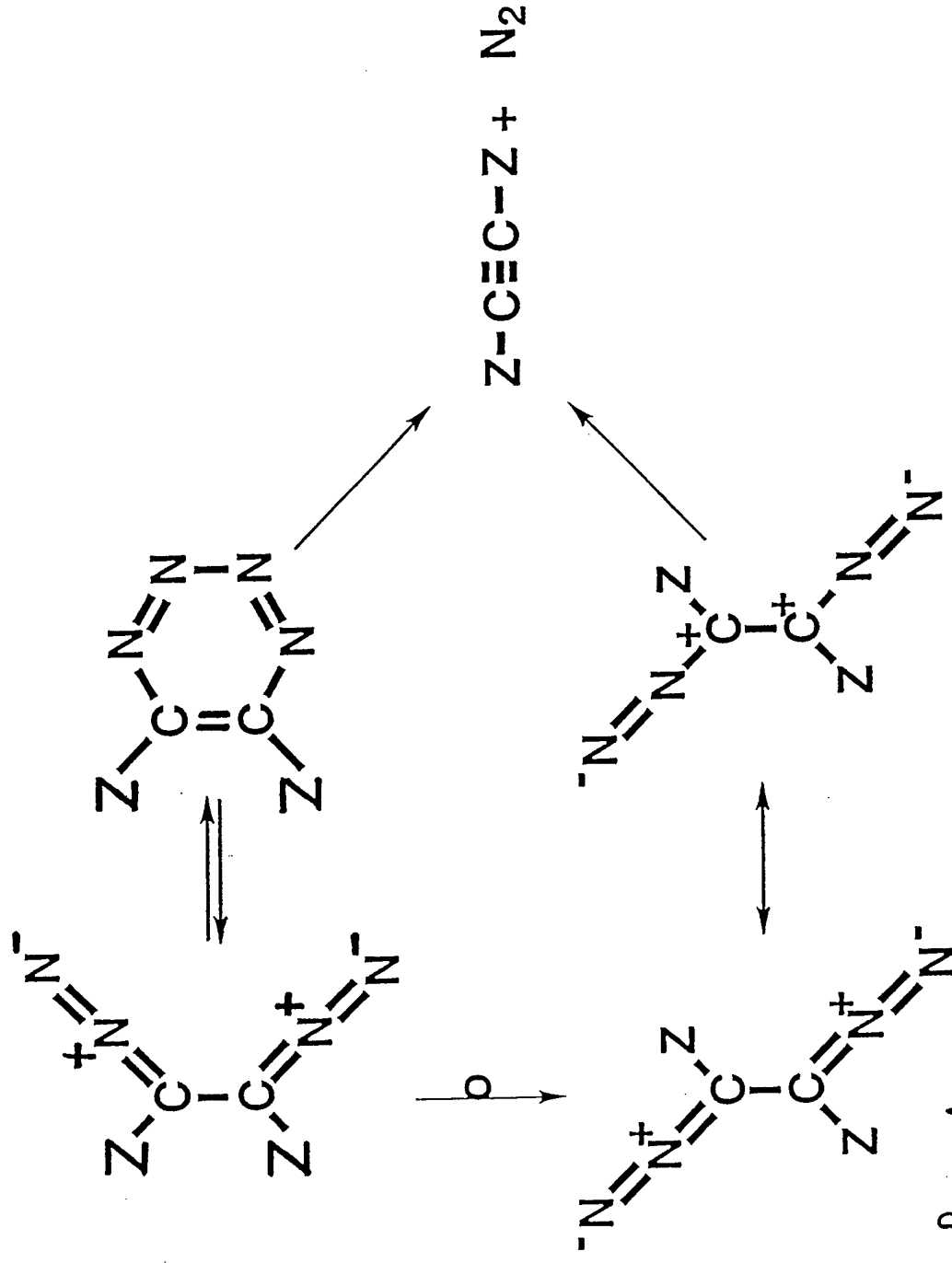


$n = 3-8$

$n = 3-8$

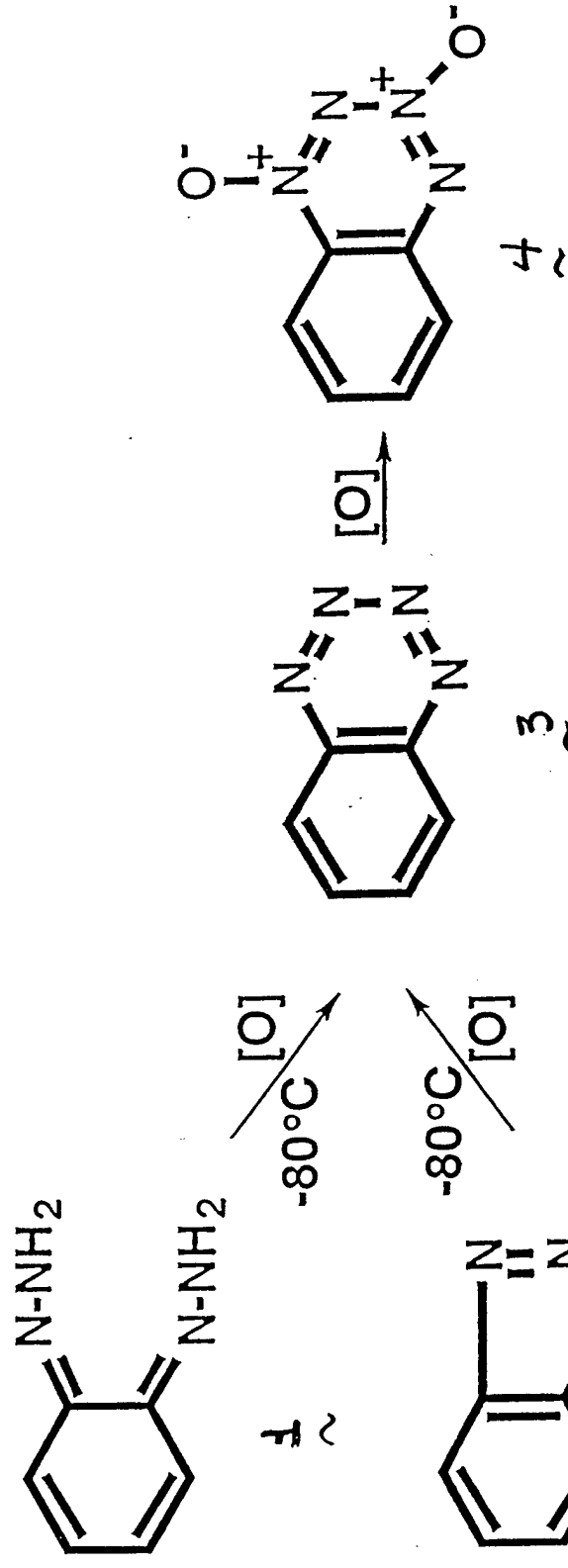
This overhead summarizes the results of oxidizing open-chain and cyclic vicinal dihydrazones with $\text{Pb}(\text{OAc})_4$, TMC, and CH_2Cl_2 . Acetylenes, even cyclopentyne, are produced in excellent yields. Of further interest is oxidation of 1,2-cyclohexanedihydrazones with $\text{Pb}(\text{OAc})_4$. Can cyclobutyne be prepared? The strain in cyclobutyne will be enormous!

Vic-Bis-diazo Compounds or 1,2,3,4-Tetrazines

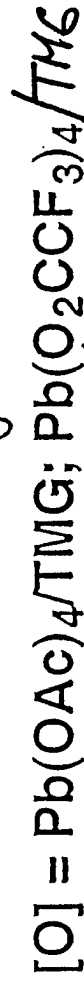


Why are vic-diazo compounds so unstable whereas mono-diazo compounds are not?
 Is stereochemistry very important? Are the 2 positive charges on adjacent carbon making the vic-diazo compounds so unstable? These results are very surprising.

Synthesis of Tetrazine 1,3-di-N-oxides

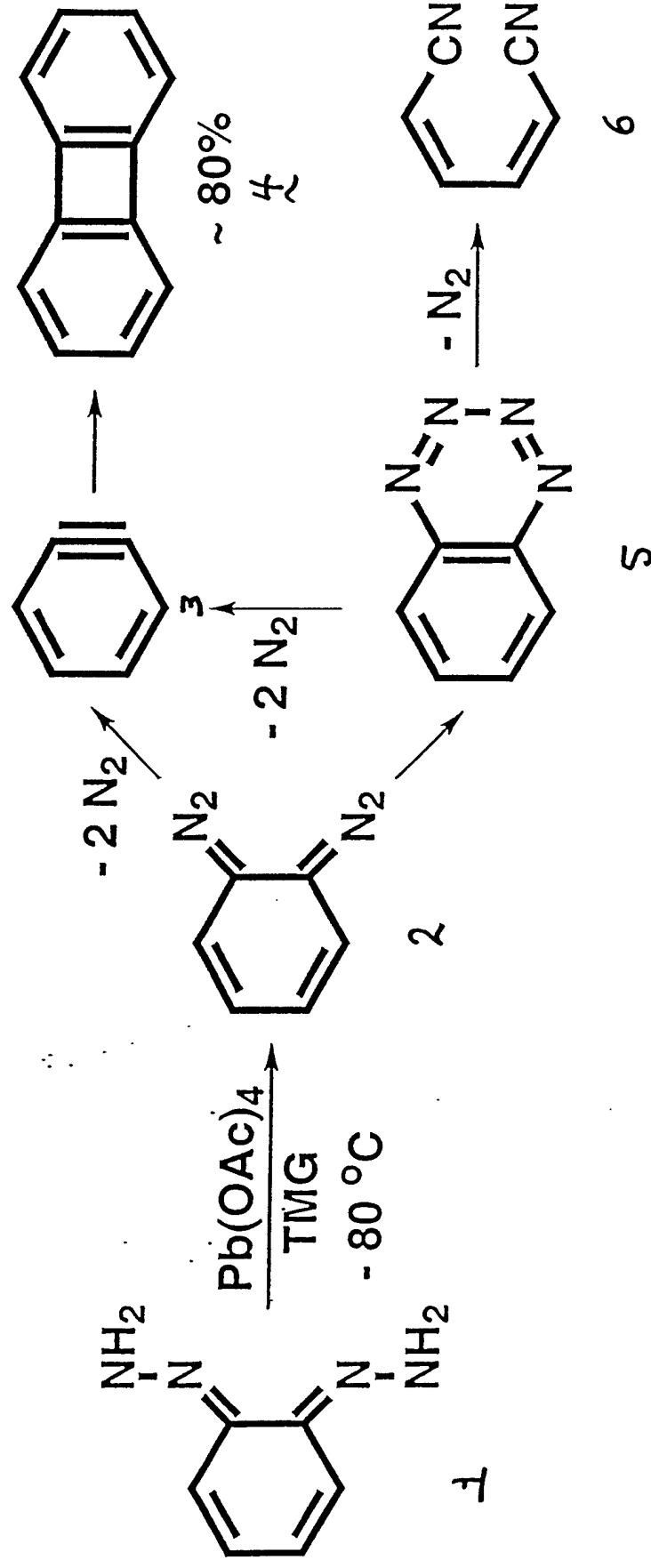


Study was initiated of possible oxidative-conversion of 1 and 2 to 3 as a possible practical source of 4. The oxidizing agent 5 is much more powerful



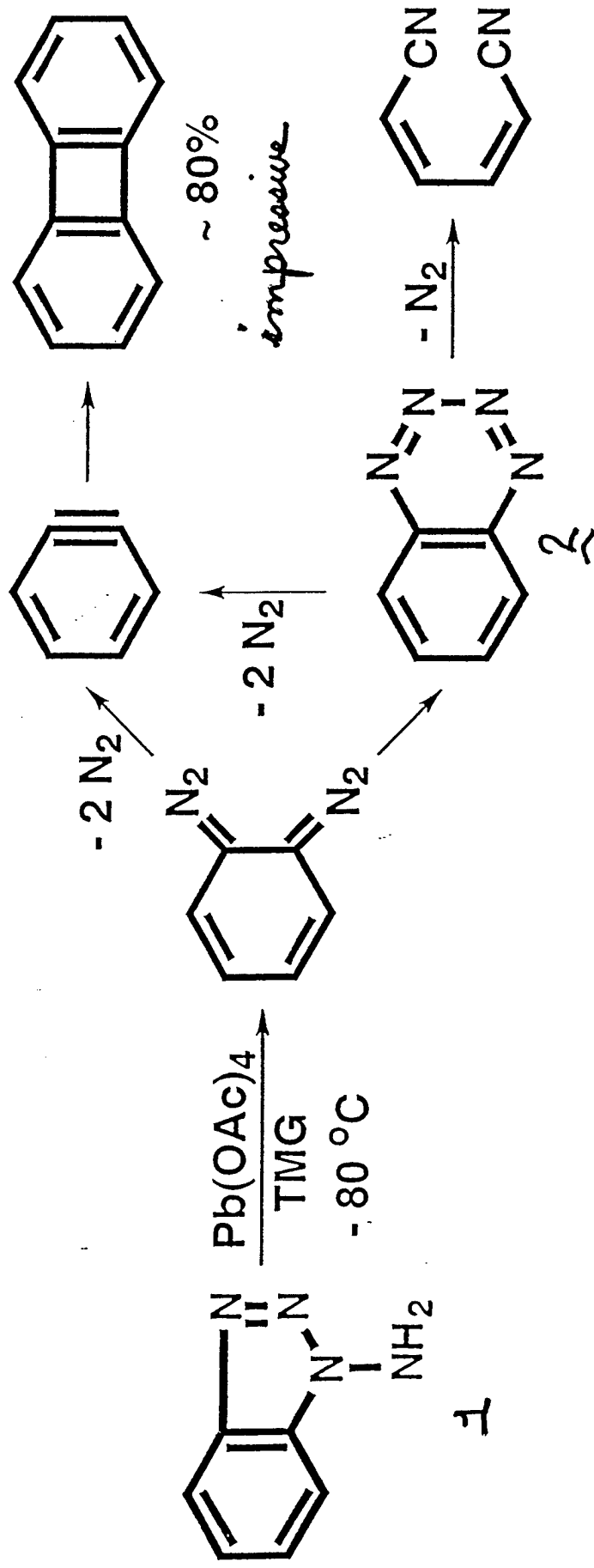
and can be used at lower temperatures than 5.

Oxidation of o-Quinone Dihydrazones with $\text{Pb}(\text{OAc})_4$



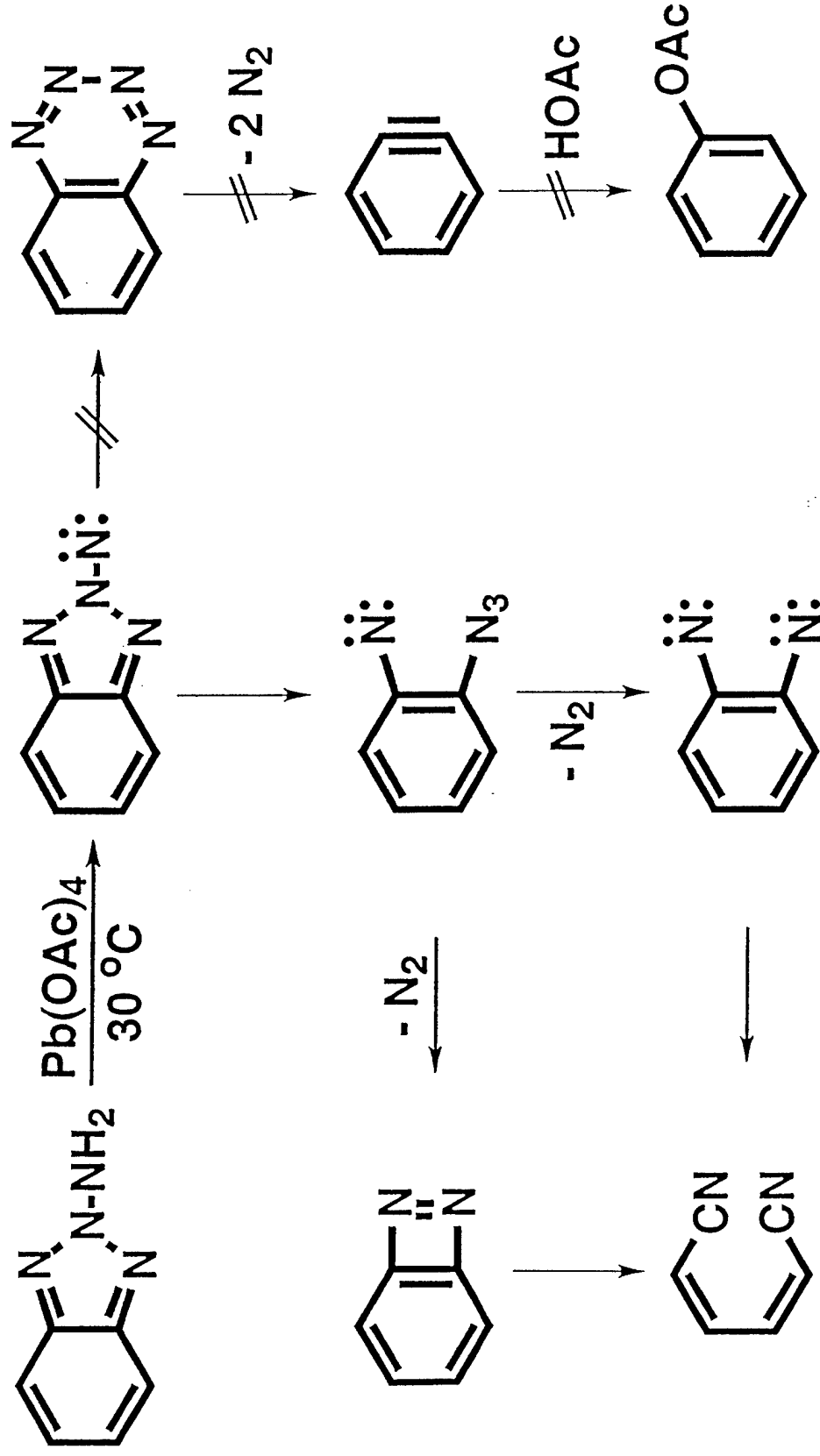
Investigation: Lower Temperatures; Solvents; IR; Oxidants; Traps

Oxidation of 1 by $\text{Pb}(\text{OAc})_4/\text{TMG}$ at temperatures as low as -100°C yields biphenylene ($\sim 80\%$) and 1,4-dicyano-1,3-dioxadiene ($\sim 20\%$). Benzotetrazine could not be detected. Can the oxidation be effected at lower temperatures?



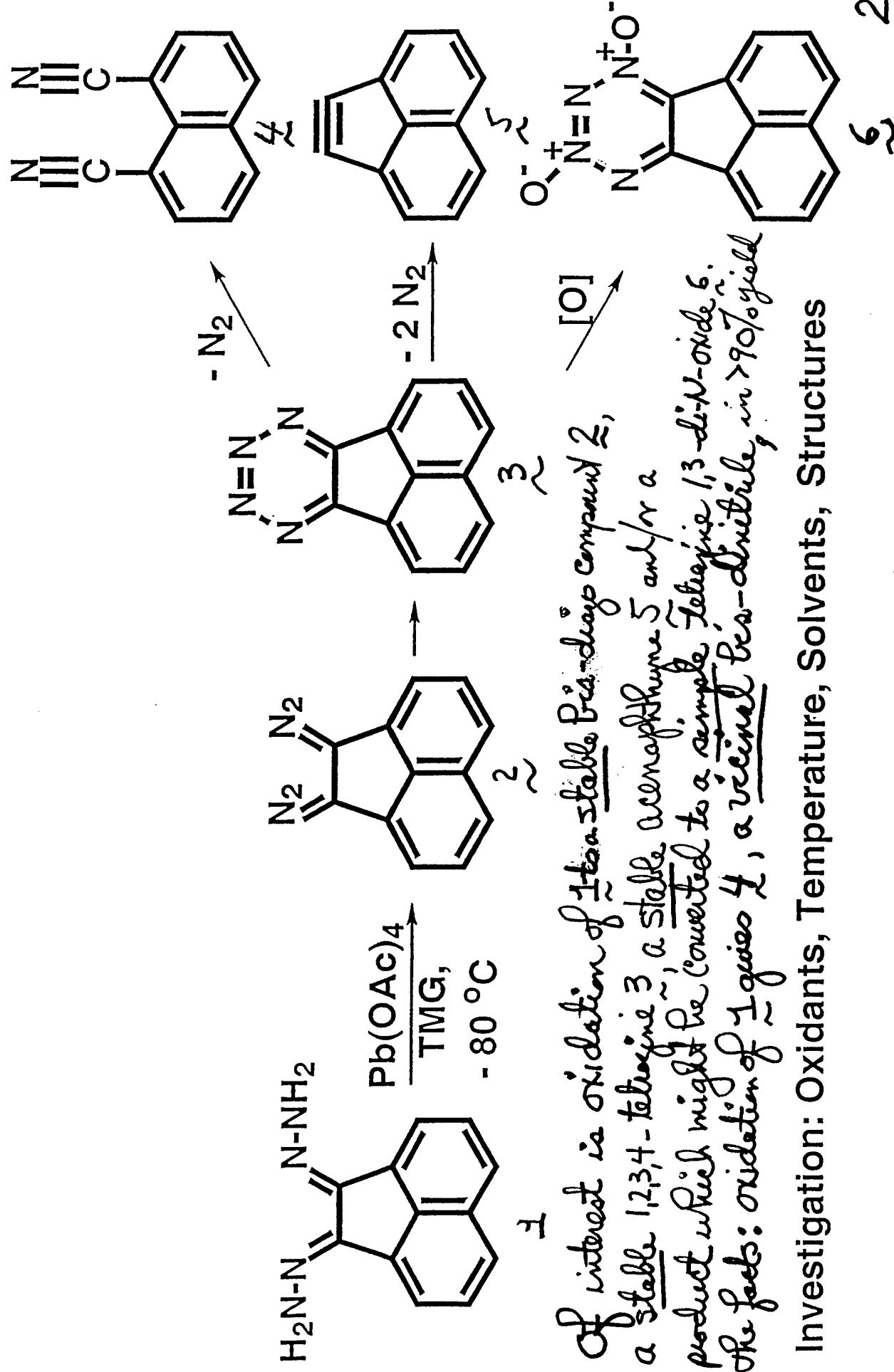
Of interest is the oxidative behavior of 1-aminobenzotriazole. Will the products of reaction of 1 be the same as in the previous overhead? The results are essentially identical; tetrazine 2 has as yet not been detected. Of note is that 1,4-dicyano-1,3-butadiene is formed!

Oxidation of 2-Aminobenzotriazole



Of interest is the oxidative behavior of 2-aminobenzotrile.
It has been presently found that oxidation of 2-aminobenzotrile
gives much more dicarbonyl-1,3-propanone than does 1-aminobenzotrile.
The reaction intermediates are different.

Oxid'n of Acenaphthenequinone Dihydrazones with $\text{Pb}(\text{OAc})_4$

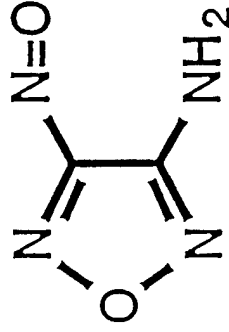


Of interest is oxidation of 1 to a stable Pis-diaz compound 2,
a stable 1,2,3,4-tetrazine 3, a stable acenaphthene 5 and/or a
product which might be converted to a simple Tetrazine 1,3-di-N-oxide 6.
The facts: oxidation of 1 gives 4, a vicinal bis-dinitrile, in >90% yield

Investigation: Oxidants, Temperature, Solvents, Structures

Furazanotetrazine 4,6-Di-N-oxide (FTDO)

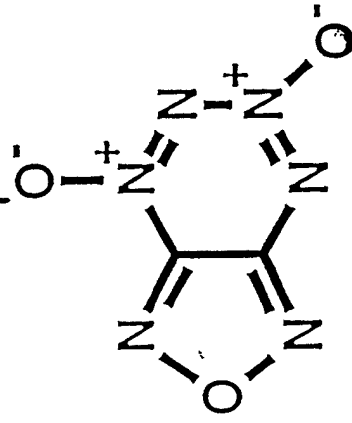
FTDO is now to be discussed because it is proposed to be useful for preparing DDTO or/and DDDTO. FTDO was synthesized in the early 90s and was minimally described in a paper cited. It takes in the early 90s and was minimally described in a paper cited. The synthesis of FTDO is in a P.D. Thesis in Moscow. I want a copy of this thesis.



The mechanism of this reaction is not known.

We will spend a lot of time on preparation of FTDO. FTDO is needed in large quantity!

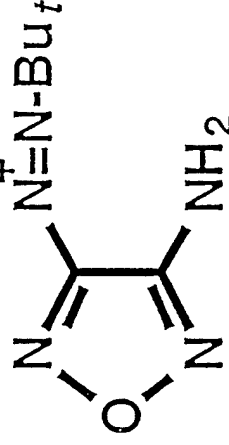
There are no x-ray data for this product!!



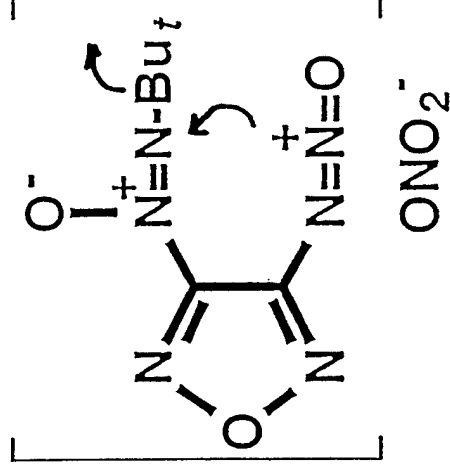
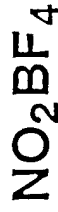
mp 110-113°

FTDO is minimally described in the paper cited. It takes in the early 90s and was minimally described in a paper cited. The synthesis of FTDO is in a P.D. Thesis in Moscow. I want a copy of this thesis.

Careful reading of this paper raises problems as to how reliable the Russian synthesis is!!



The nitramine is just generated when then loses OT to give the intermediate below.



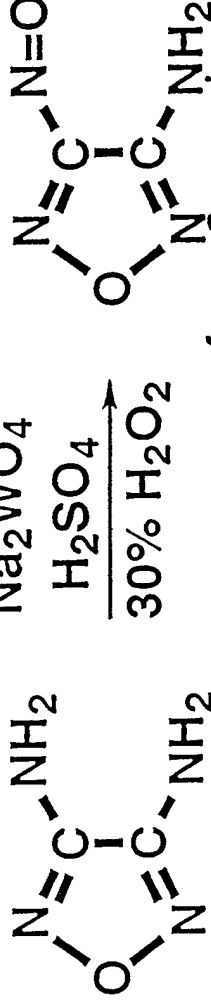
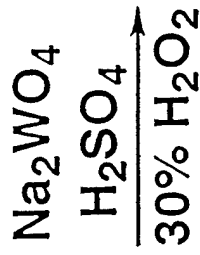
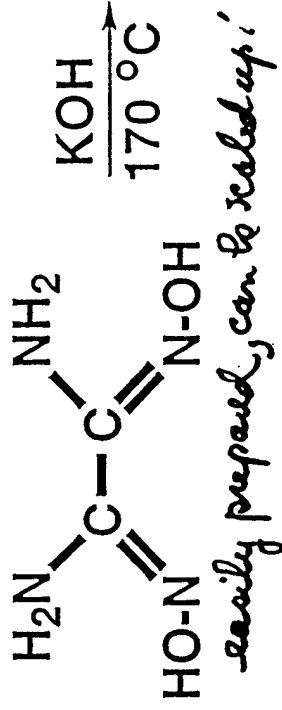
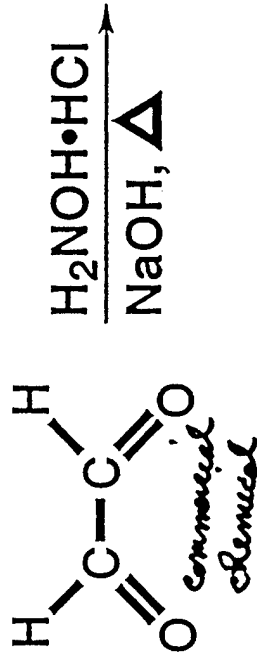
note the methodology for any closure! This is superb chemistry, if correct, of

Churakov et al, Tetrahedron, 1995

The method for preparing FTDO is based on that to be described much later for benzotetrazine 1,3-di-N-oxide.

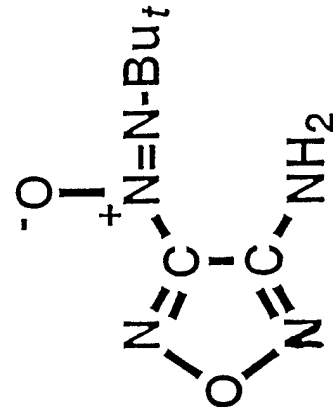
This is a summary of the Russian and now a OSA synthesis of FTD. Preparation of FTD has been difficult! The CIA for somebody should have scanned a Russian thesis describing the final step in the synthesis.

Furazanotetrazine 4,6-Di-N-oxide (FTDO)

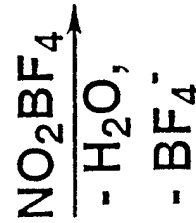


adiazine of great interest to the Air Force! Edwards!

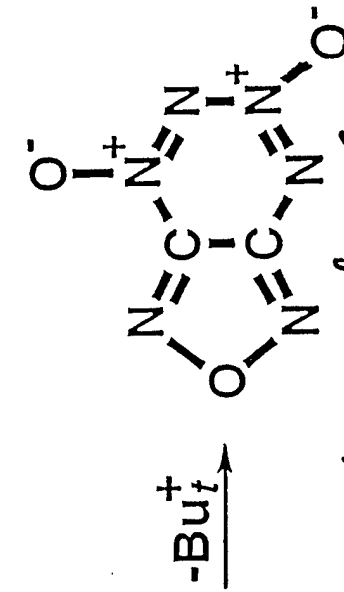
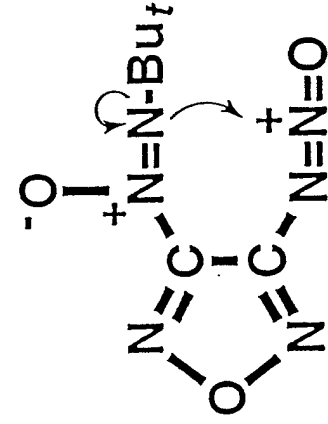
We at OSA have improved synthesis of this nitroamine!



There have been problems in this step! To scale up this step satisfactorily is questionable!



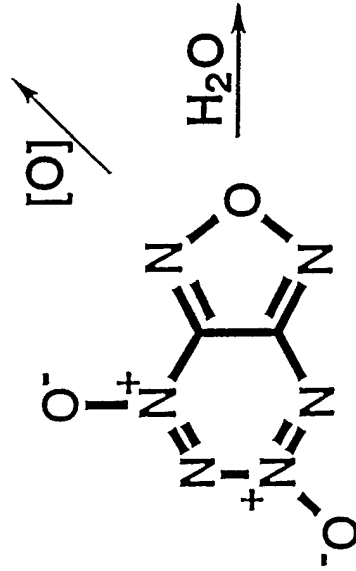
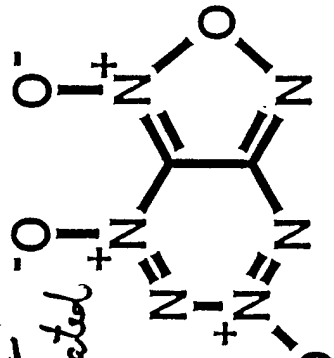
We like $\text{N}_2\text{SO}_2\text{CF}_3$ much better than N_2BF_4 . Expensive at present.



X-ray analysis of FTD has not been successful. The crystals have not been satisfactory!

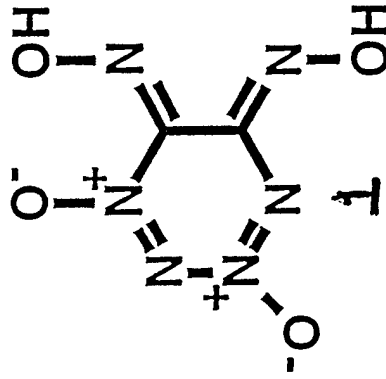
The following transformations of FTD

have not been successful. These reactions are believed to be investigated in Moscow. This study needs much stronger support and should be discussed in much greater detail. Where are the Russians in these areas? ²-O

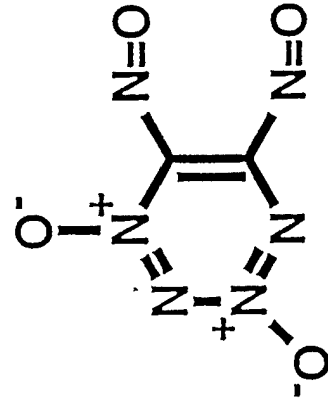


[O]

H₂O

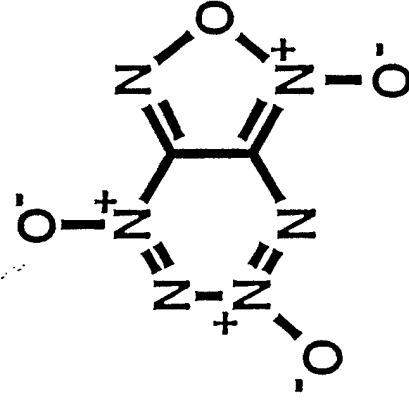


[O]



acid- and base-catalyzed hydrolyses of FTD give many products.

[O]

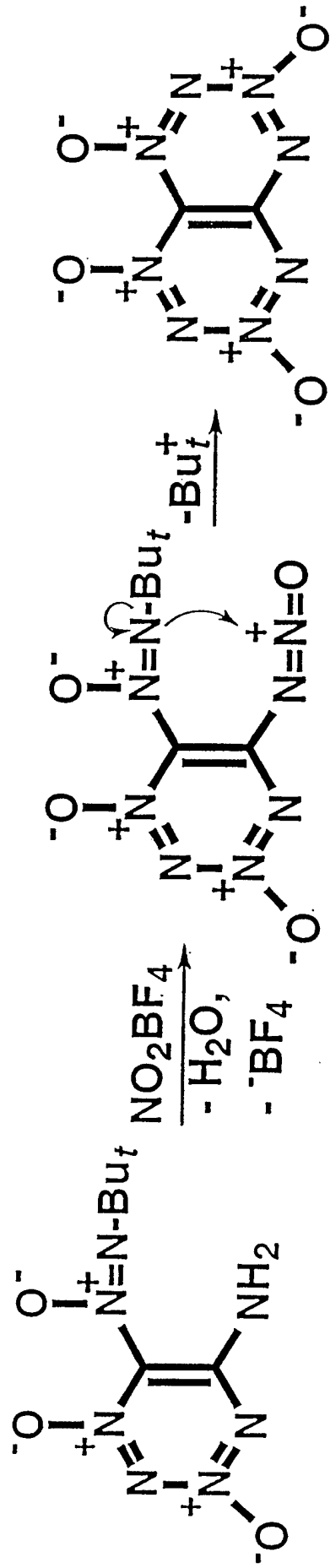
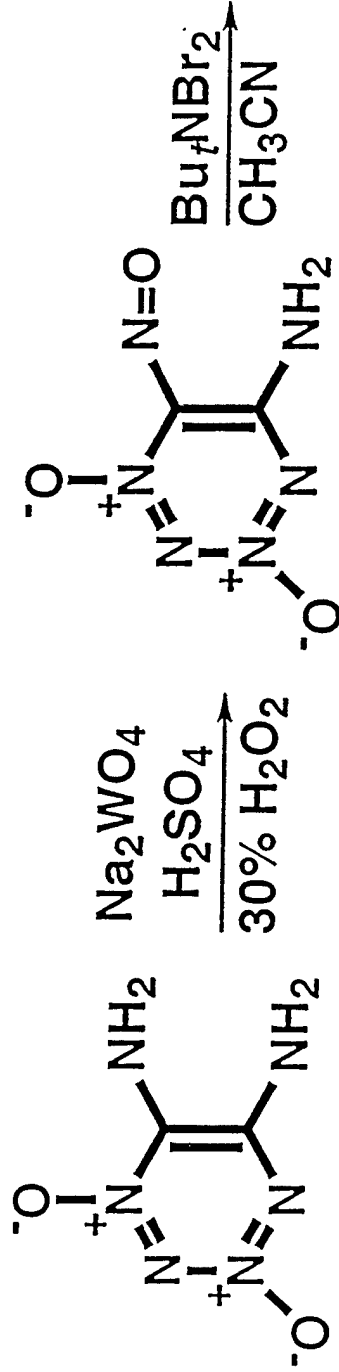
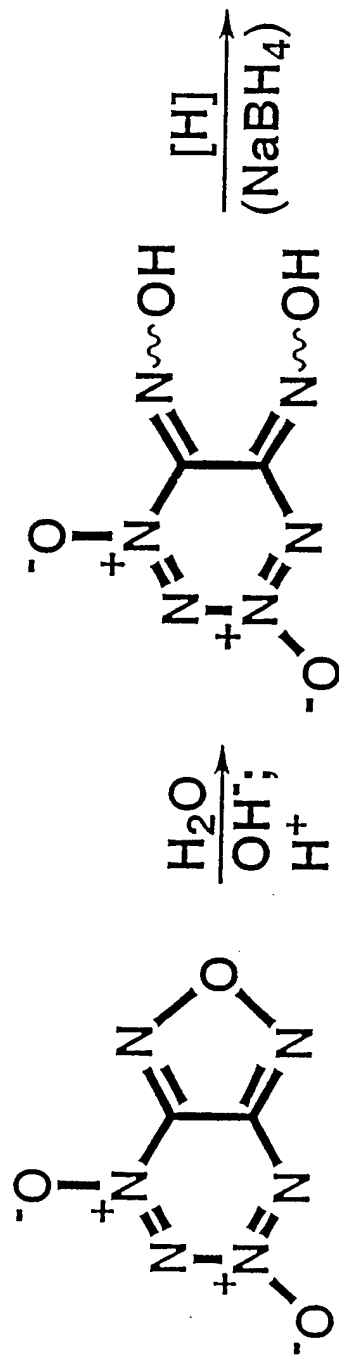


If 1 can be prepared as indicated, this approach to synthesis of DTD a/and S-DTD could be practical.

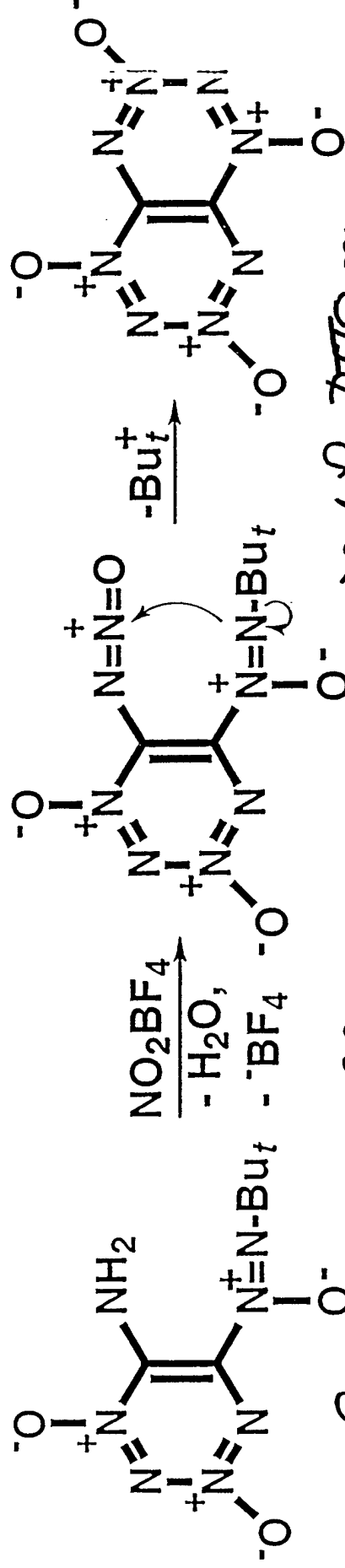
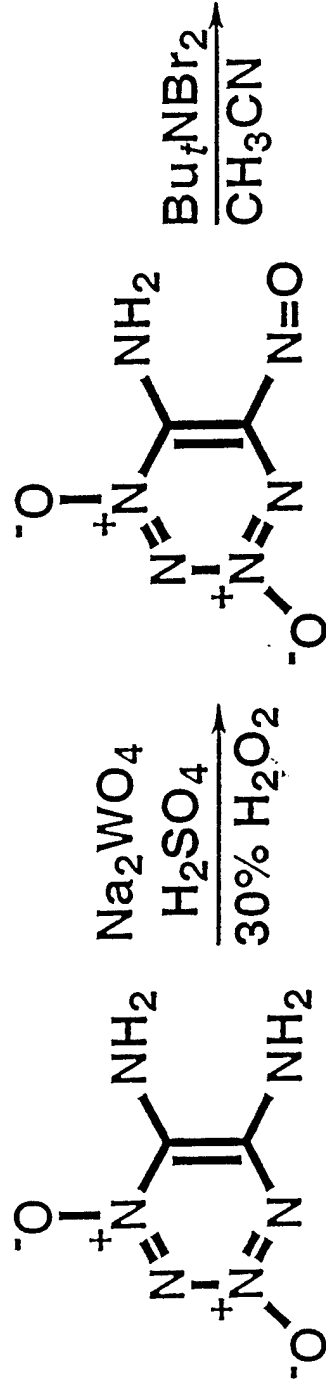
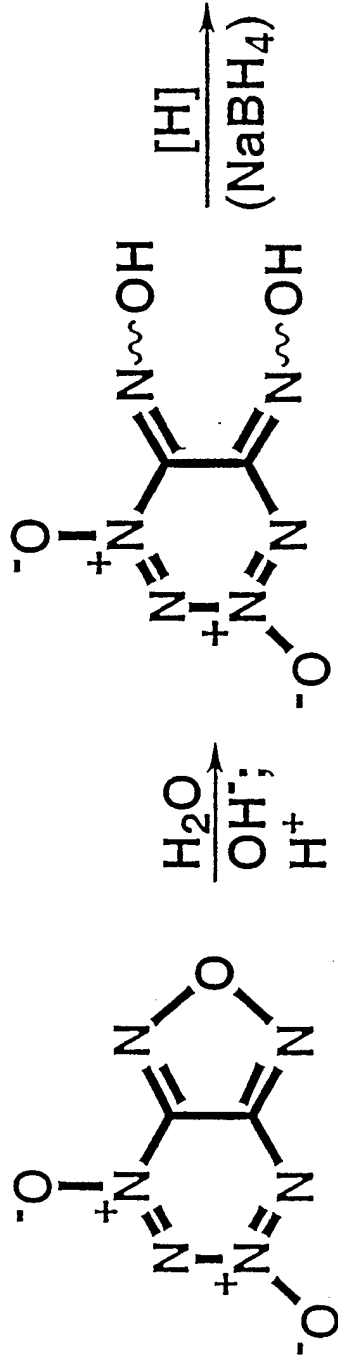
This is an important project! We have not had sufficient support to investigate the above project properly. Zelinski" has had a 10-12 year head start on this work.

This overhead summarizes the present route proposed for DTTO at OSEI.
 Are the Russians studying this route? We believe so.

Proposed Synthesis of DTTO

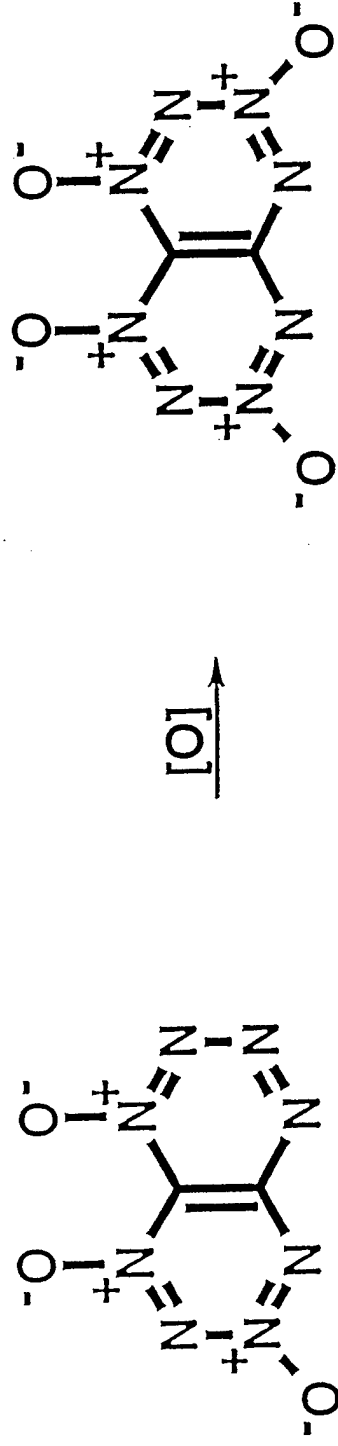
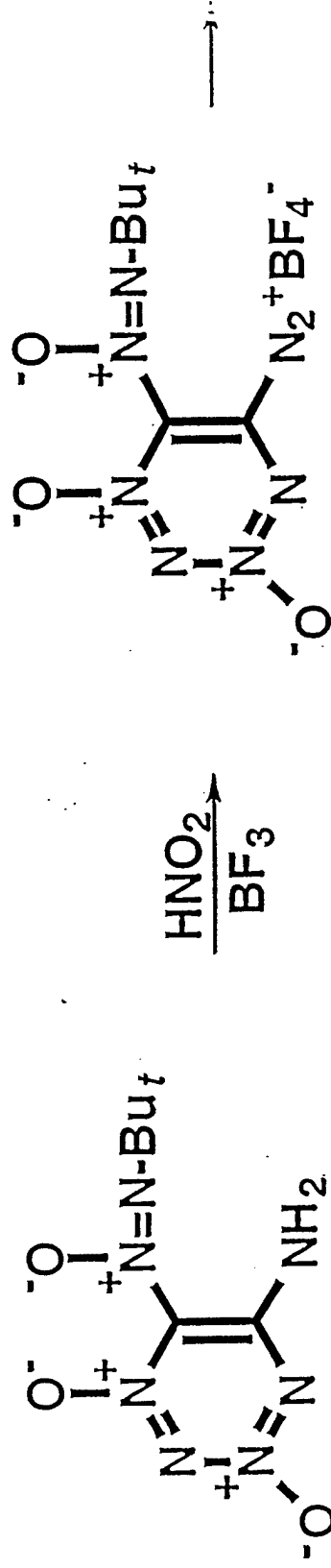


Proposed Synthesis of IsoDTTO



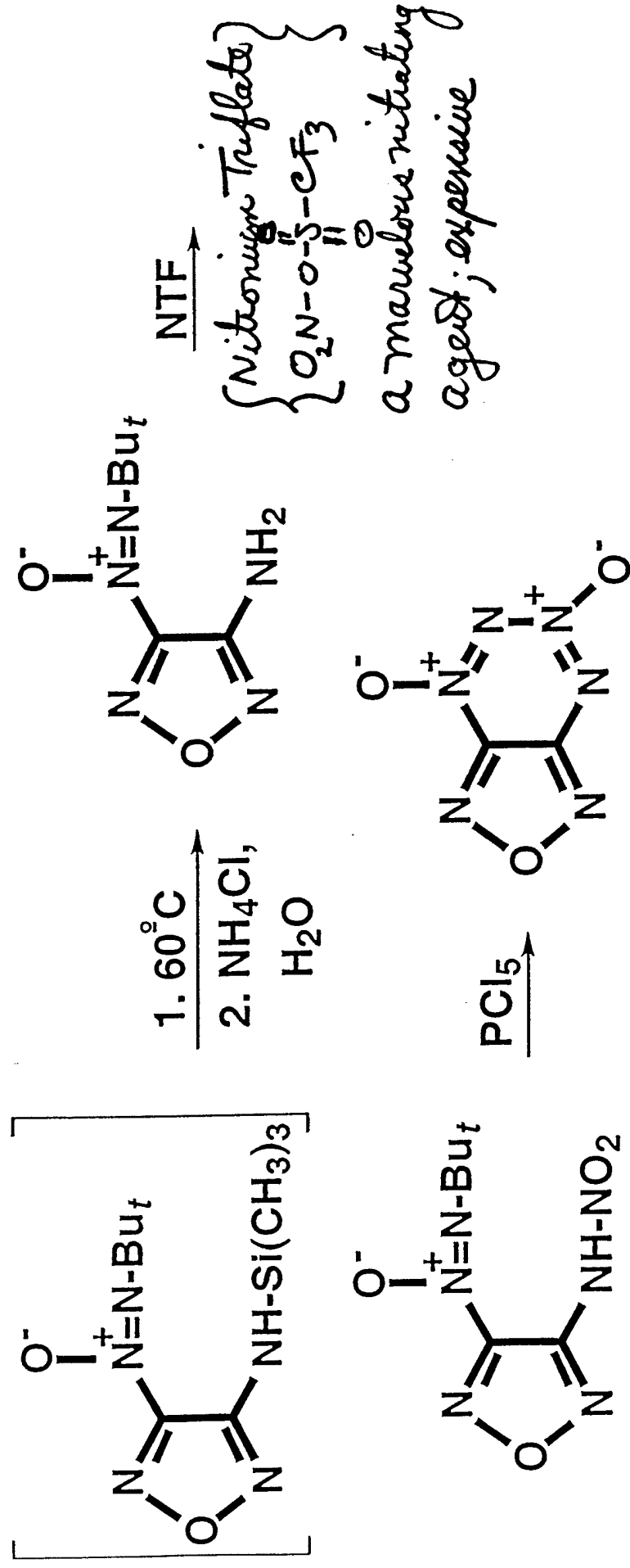
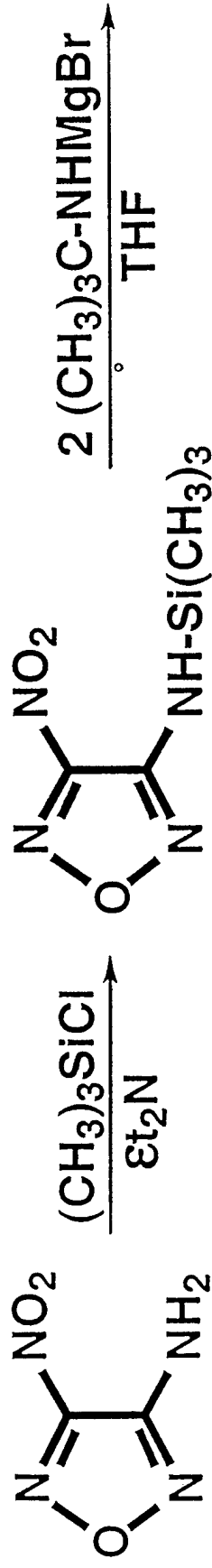
This synthesis of IsoDTTO parallels that for DTTO on the previous overhead. The key is successful ring-opening of FTDG!

Proposed Synthesis of DTTO



This is an alternate synthesis of DTTO. This ring-closure is different than that proposed previously. This sequence also proposes initial preparation of a 1,2,3,4-tetrazine-1-oxide which is stable.

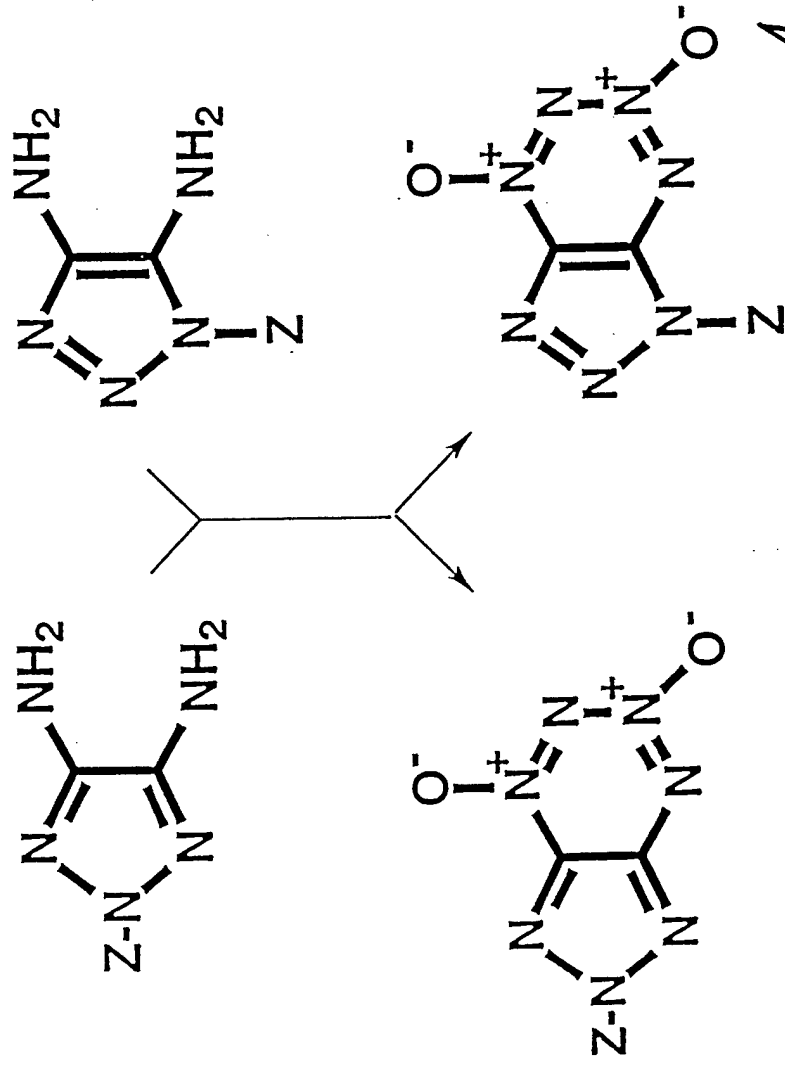
Furazanotetrazine 1,3-Di-N-Oxide



OHIO STATE

This is a major advance in synthesis of FTD!

Synthesis of Triazolotetrazine 1,3-Dioxides

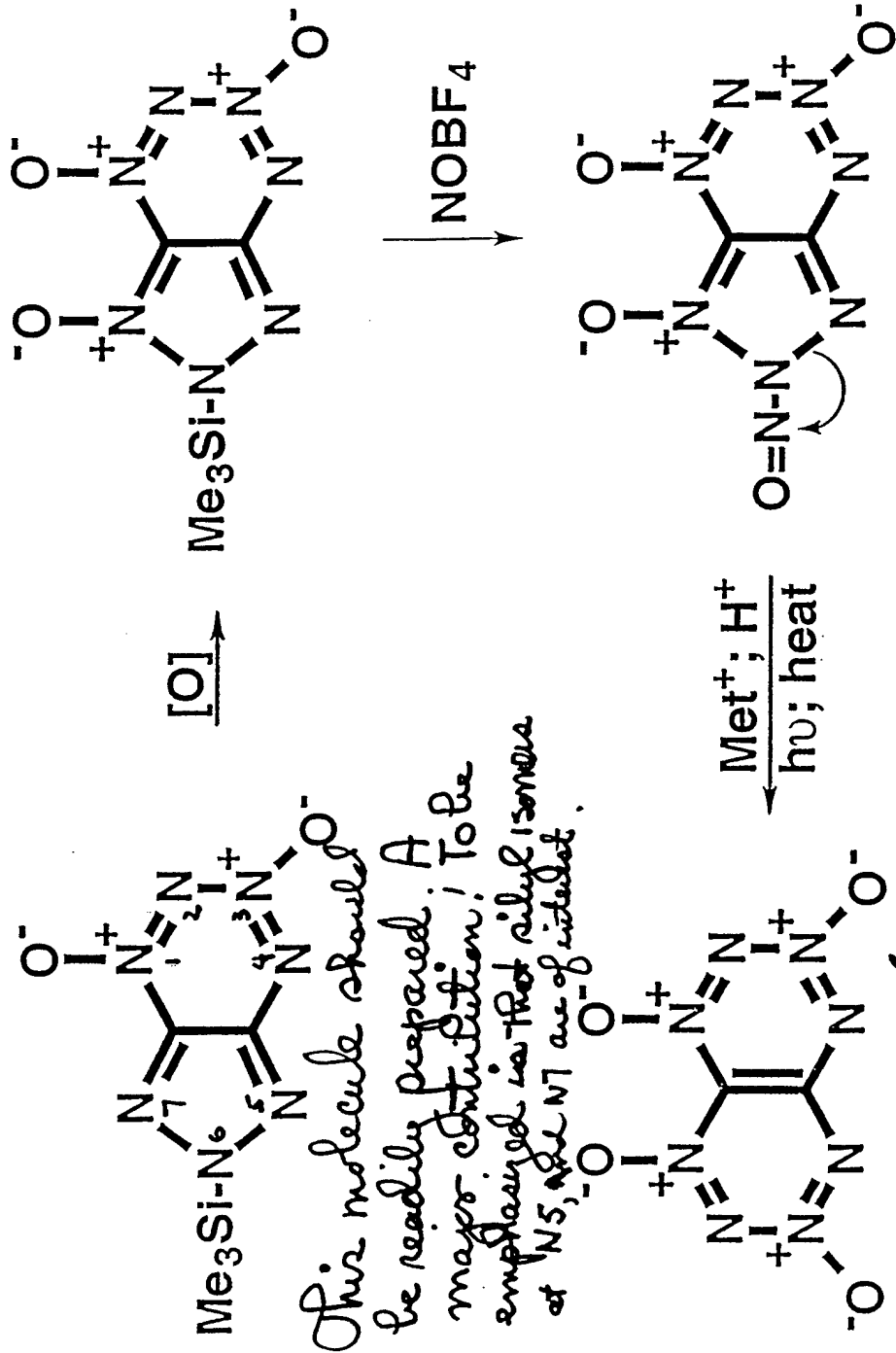


*Are these sequences
being investigated
in Russia?*



*These synthesis routes are now to be studied.
This effort will have to be funded soon.
Very practical chemistry might come from these sequences.
These sequences have been initiated at ORL.*

Possible Synthesis of DTTO

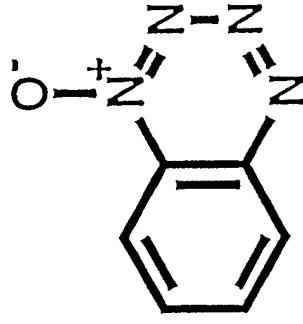
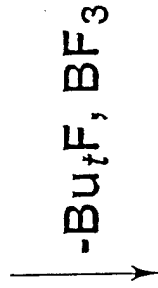
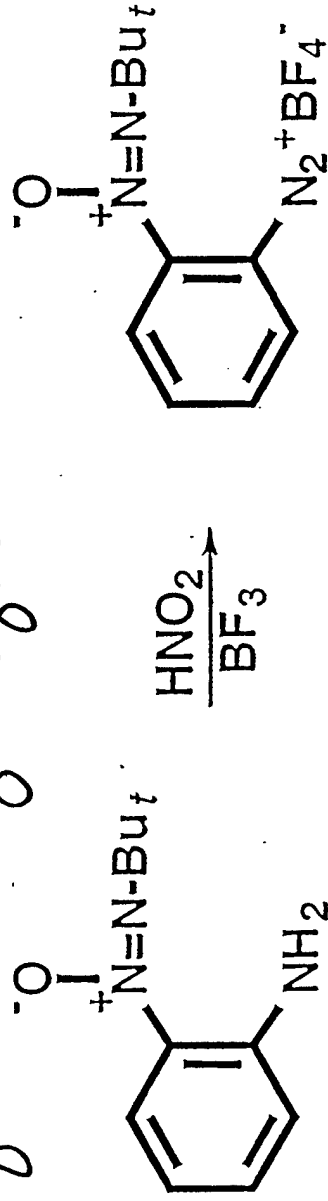


This molecule should be readily prepared. A major contribution! To be emphasized is that silyl isomers at N5, and N7 are of interest.

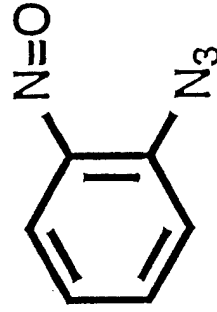
A possible practical synthesis of DTTO as yet not investigated. This is a major and important project. To be discussed further if possible

Synthesis of Benzotetrazine 1-N-Oxide

This overhead illustrates the first publication by Zelinsky for synthesis of a stable benzotetrazine oxide!



We know little about o-nitroso azides.

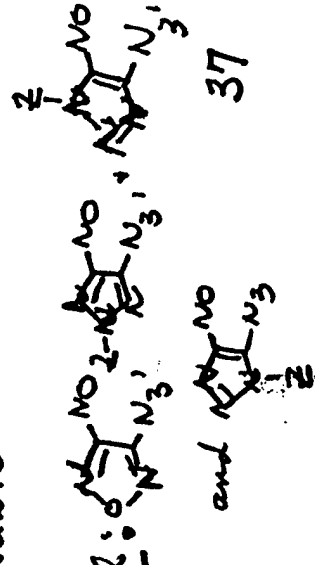


This is an important concept.

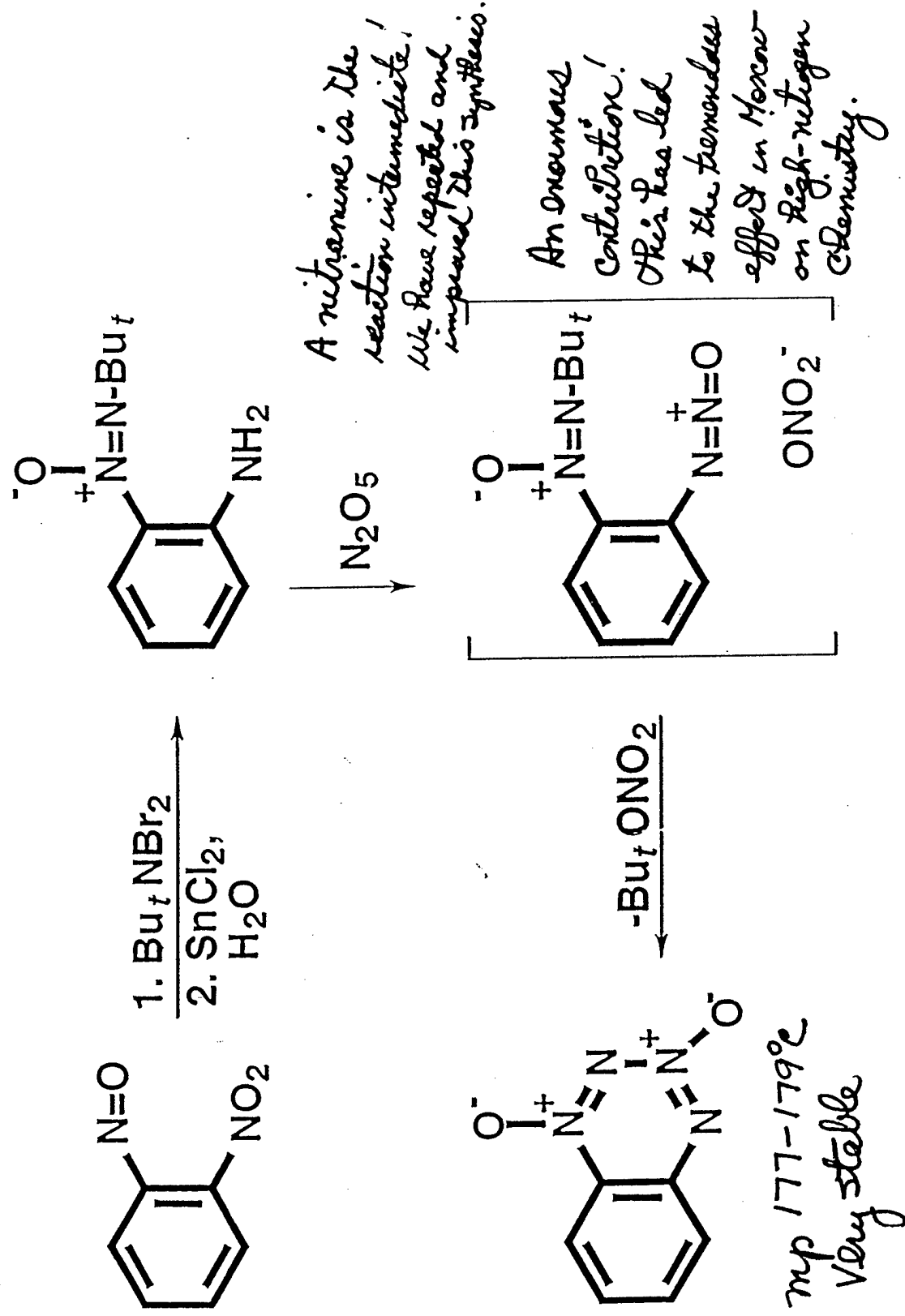
Various heterocyclic (5 and 6-membered

ring) ortho nitroso azides should be evaluated:

Do the molecules proposed exist in ring-open or ring-closed forms?

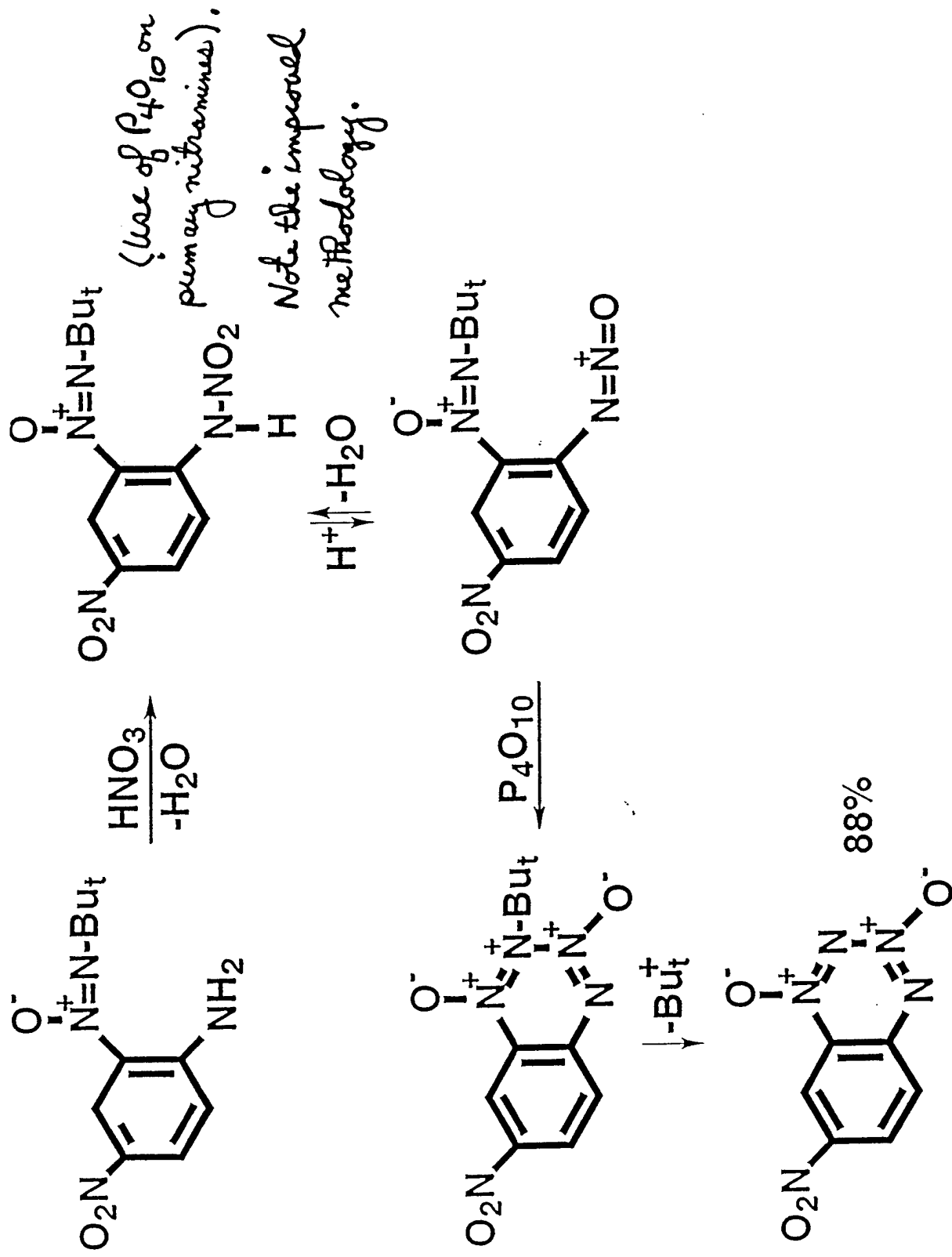


Synthesis of Benzotetrazine 1,3-Di-N-oxide



Churakov, Mendel. Comm. 1991

This is a very important paper, that was ignored in the US.

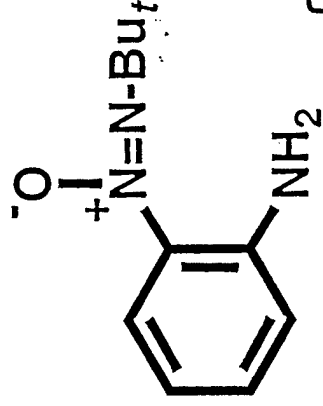
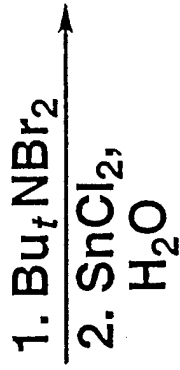
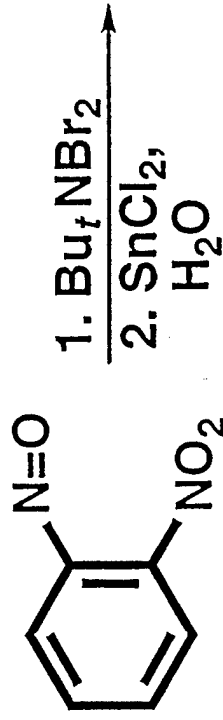


Frumkin et al, *Russ. Chem. Bull.* 2000, 49, 482

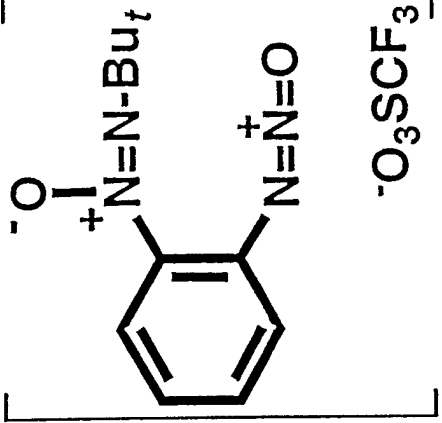
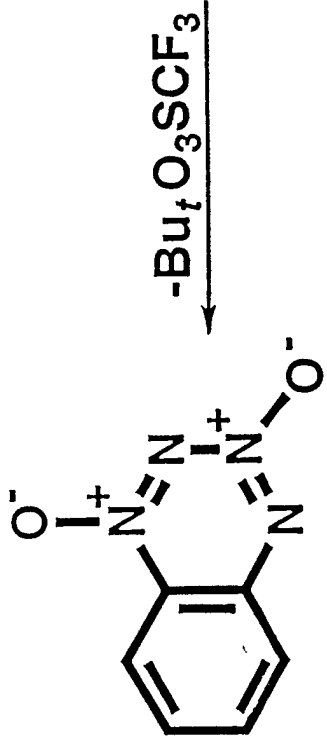
This publication extends and improves the previous methodology for preparing benzotetrazine 1,3-di-N-oxides.

Synthesis of Benzotetrazine 1,3-Di-N-oxide

an improved synthesis of benzotetrazine 1,3-di-N-oxide



study is to be made of synthesis of $\text{O}_2\text{NO}_3\text{SCF}_3$ from NaN_3 and $\text{CF}_3\text{SO}_2\text{Cl}$!! (Much cheaper)



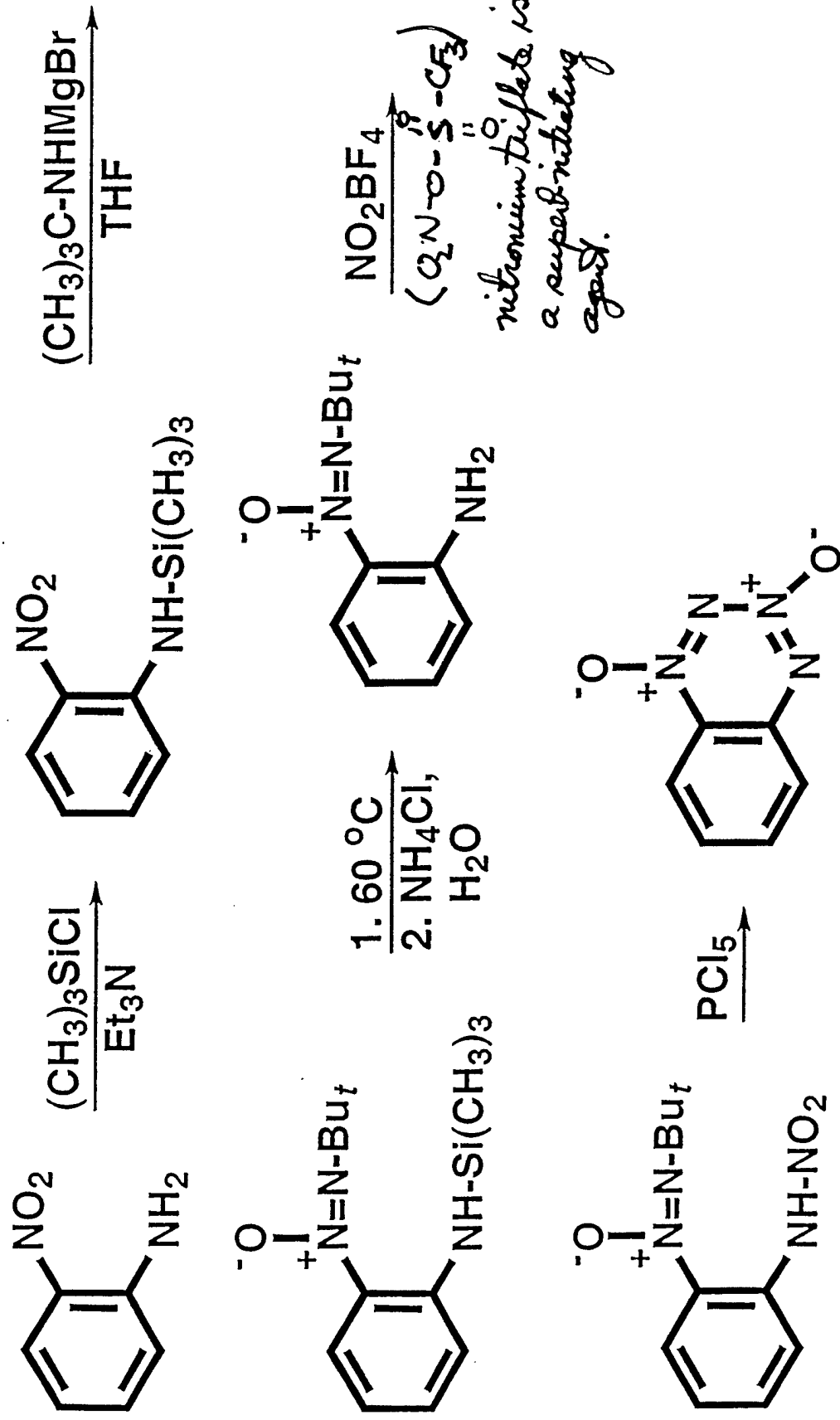
Nitronium triflate is generated from $(\text{CH}_3)_4\text{N}^+\text{NO}_3^-$ and $(\text{CF}_3\text{SO}_2)_2\text{O}$; the Stackelford method.

OHIO STATE, 2003

The major contribution at OSU is use of nitronium triflate.

Benzotetrazine 1,3-Di-N-oxide

A new method for preparing benzotetrazine 1,3-di-N-oxide

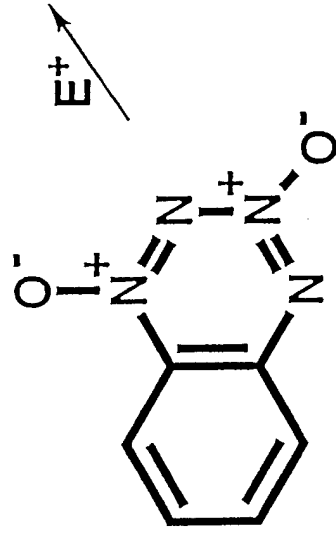


OHIO STATE

A good method developed by Dr. Venugopal for preparing benzotetrazine 1,3-Di-N-oxide,

Substituted Benzotetrazine 1,3-di-N-oxides

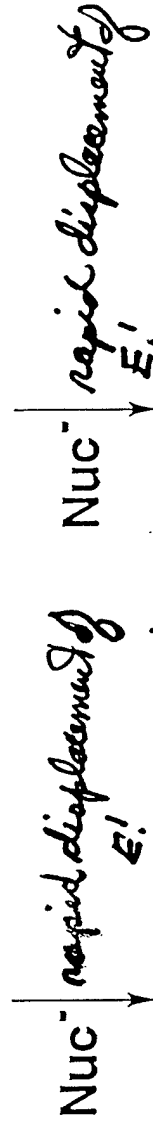
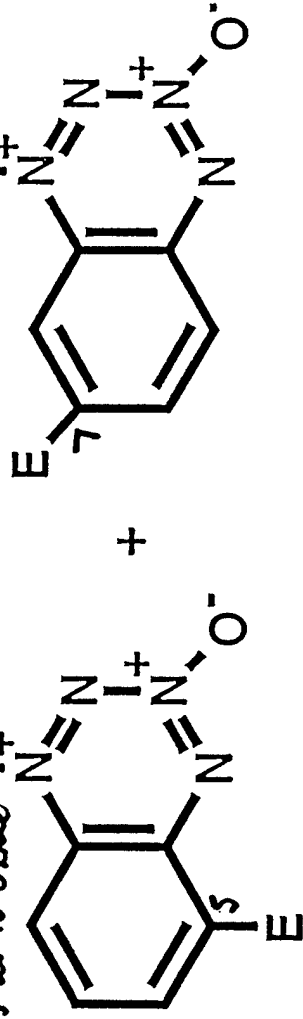
Moscow has studied in depth electrophilic substitutions of benzotetrazine 1,3-di-N-oxides. Electrophilic substitution O^- occurs preferentially at the 5 and 7 positions. The tetrazine 1,3-di-N-oxide ring stays intact.



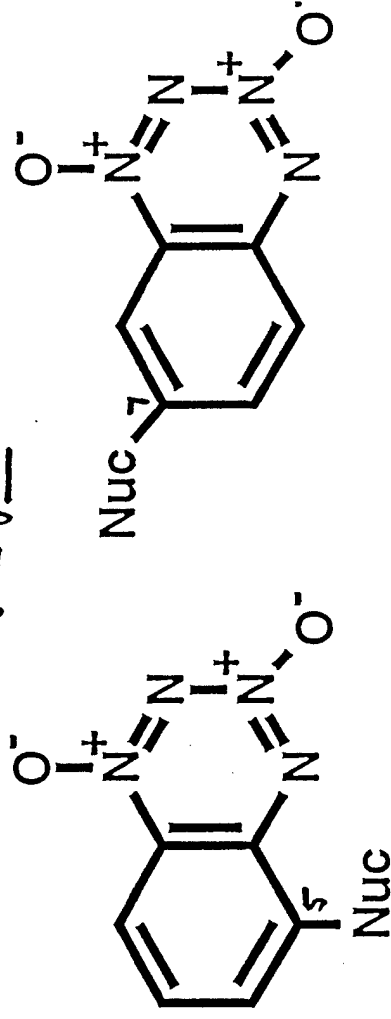
The C_5 and the C_7 substituted benzotetrazines undergoes electrophilic displacement by various nucleophiles. The behaviors of halobenzotetrazine 1,3-di-N-oxides are similar to that of picryl bromide and 1-fluoro-2,4-dinitrobenzene.



$Nuc^- = OH^-, OAc^-, OSiR_3^-, and NH_2^-$ as displacement nucleophiles have not been reported by Moscow!

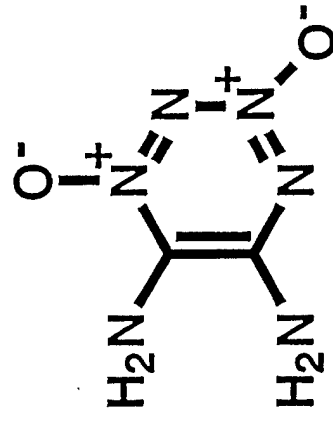
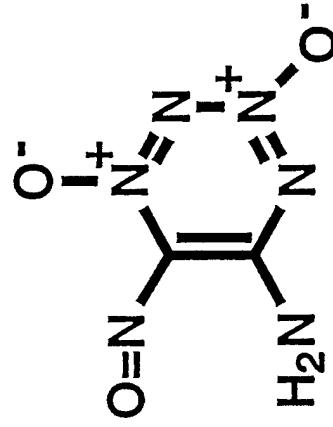
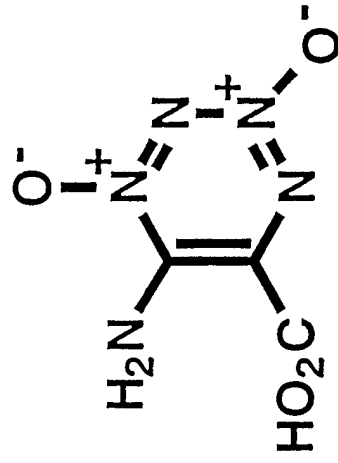
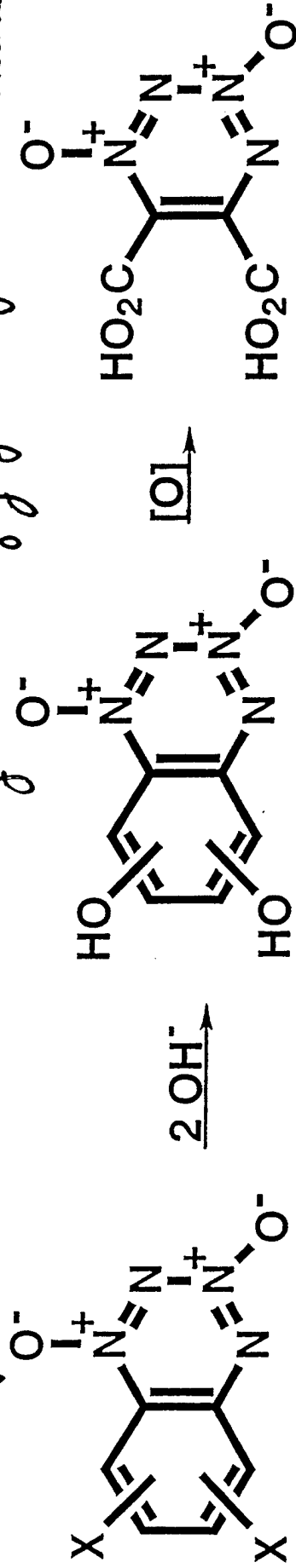


good yields

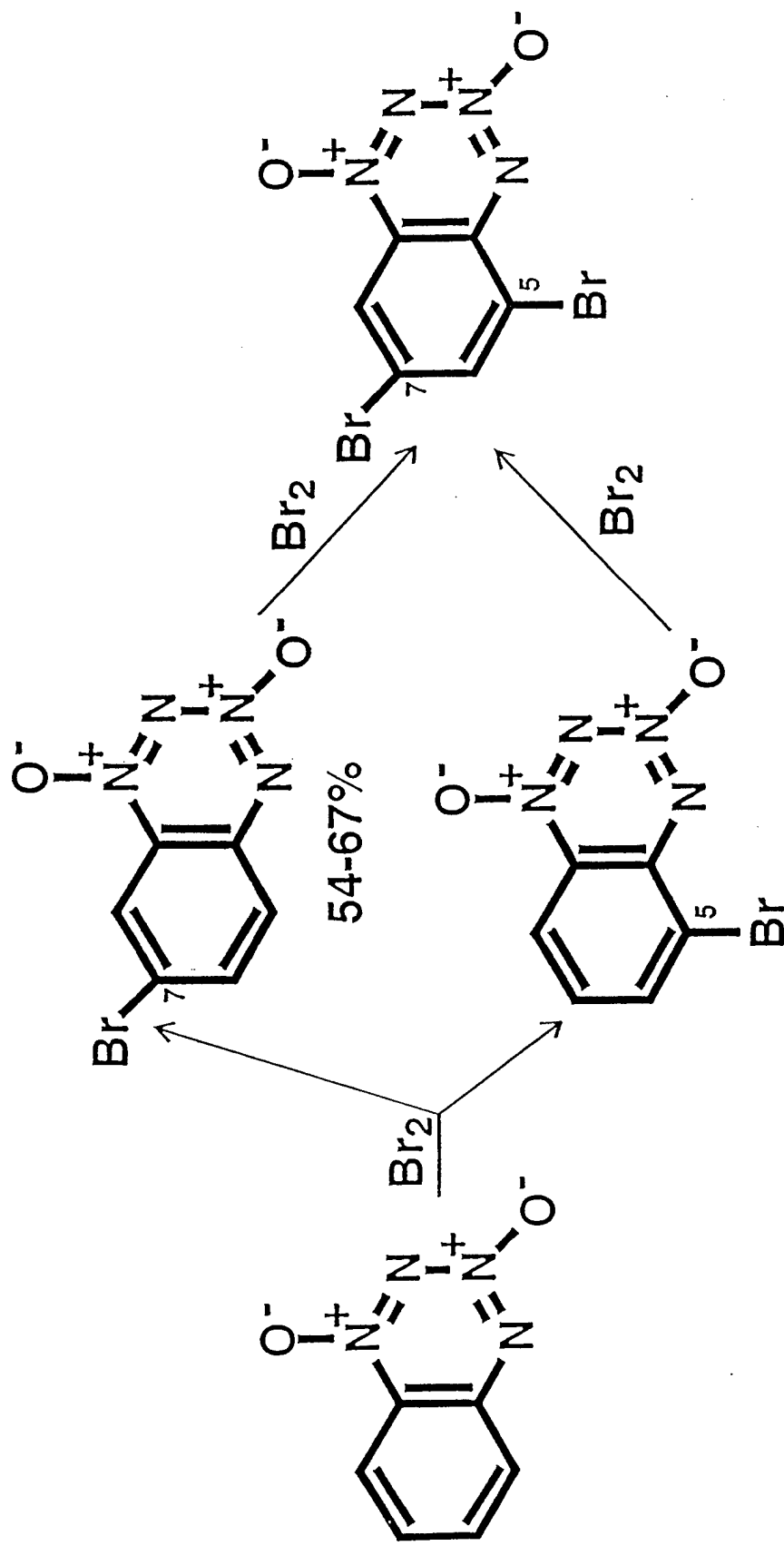


Synthesis of 1,2,3,4-Tetrazine-1,3-di-N-oxides

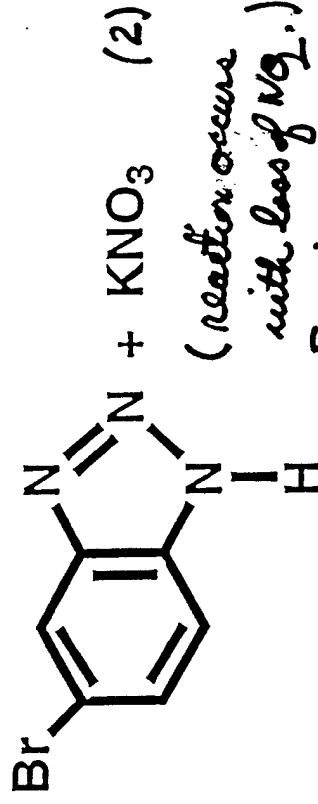
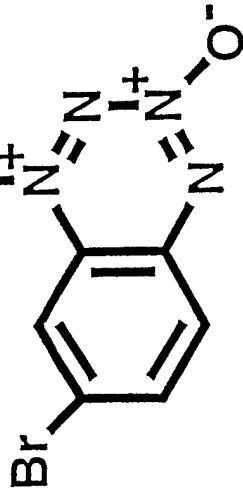
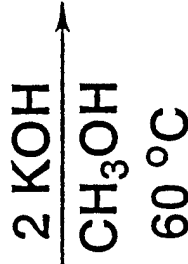
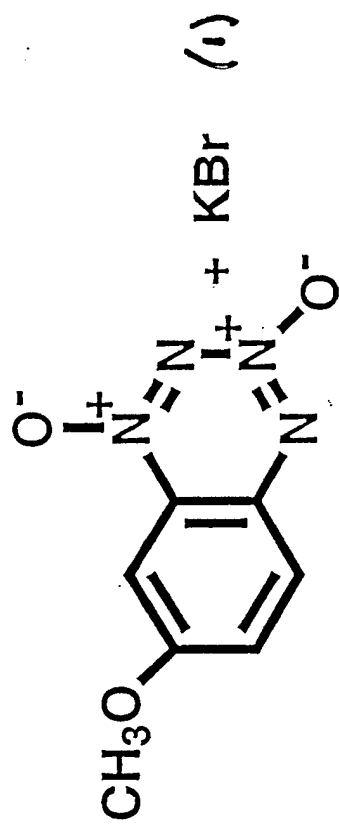
The following displacements and subsequent reactions are principal present objectives of JSC at present. Many different oxidizing agents might have to be studied



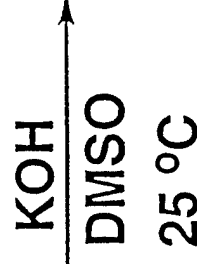
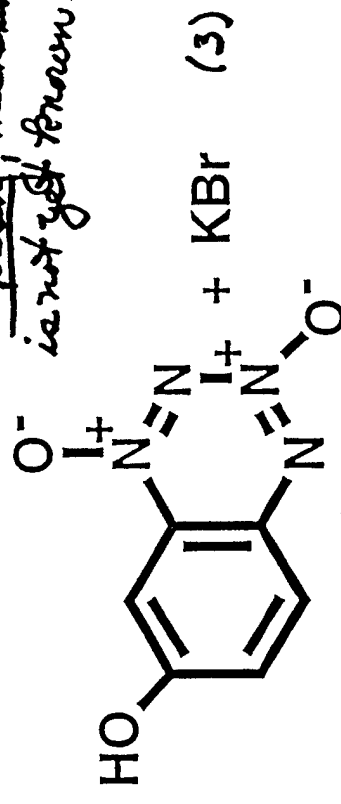
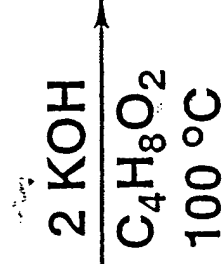
Can mono-1,2,3,4-tetrazine-1,3-di-N-oxides be prepared?
Are they sufficiently stable for subsequent use for synthesis of DTTO and for ISO-DTO? The fundamental physical-organic chemistry of such materials need determination.



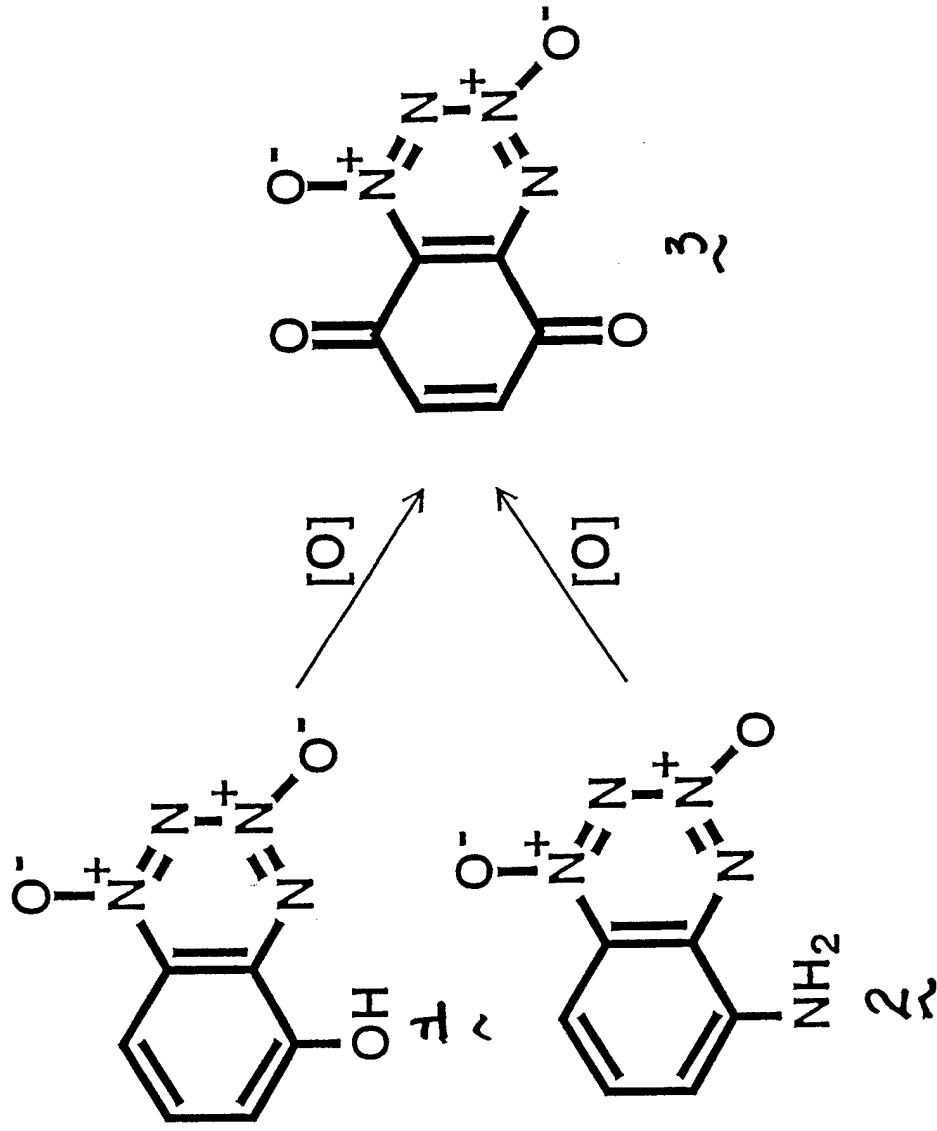
These reactions have been studied at OSE. They work well and the products are readily separated and quite stable. Present results agree with that communicated by Maslov.



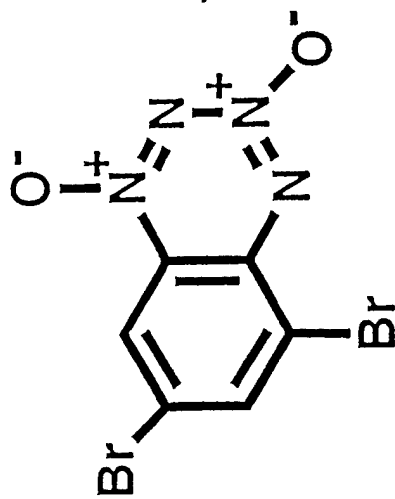
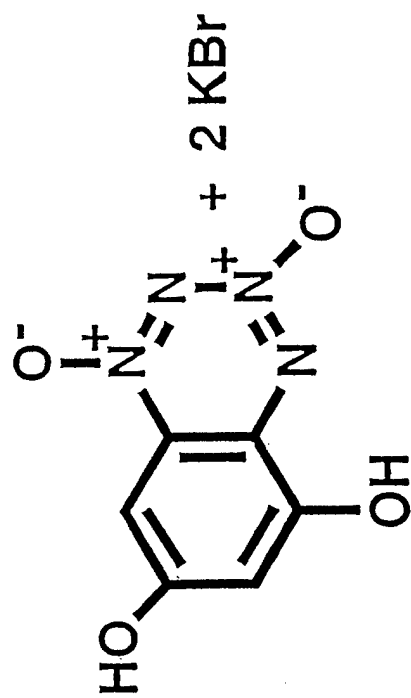
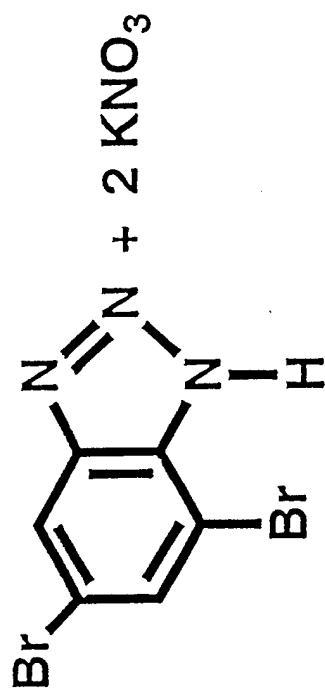
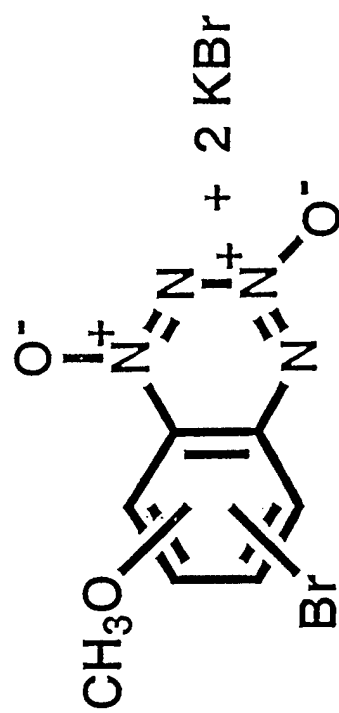
(reaction occurs with loss of NO_2 .)
Surprising; mechanism is not yet known!

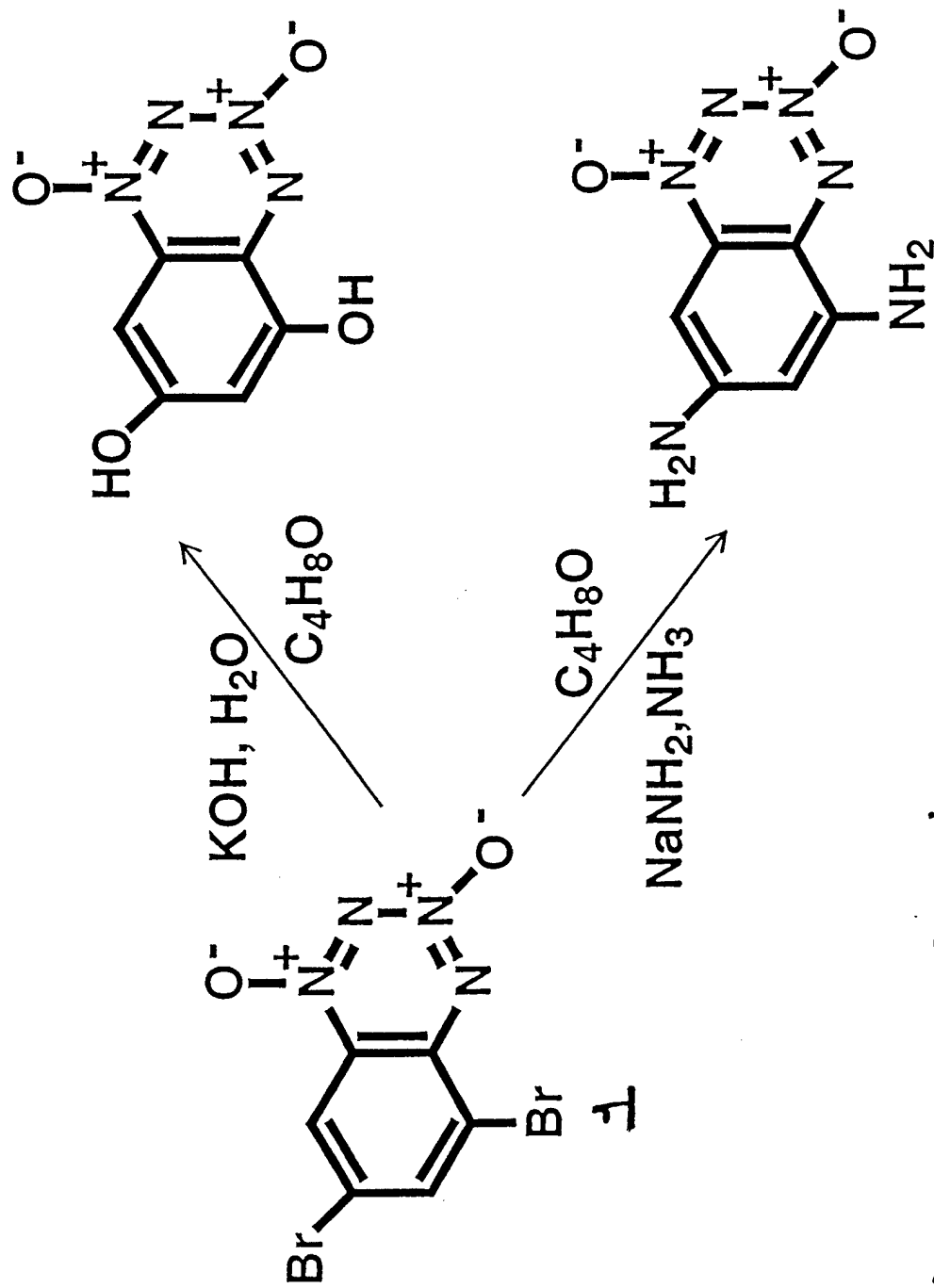


These reactions are being studied at ORU. Reaction 1 occurs as expected.
 Reaction 2 using KOH at 100°C occurs surprisingly to give the indicated triazole.
 Reaction 3 at 25°C occurs well. This low temperature reaction will be studied further.

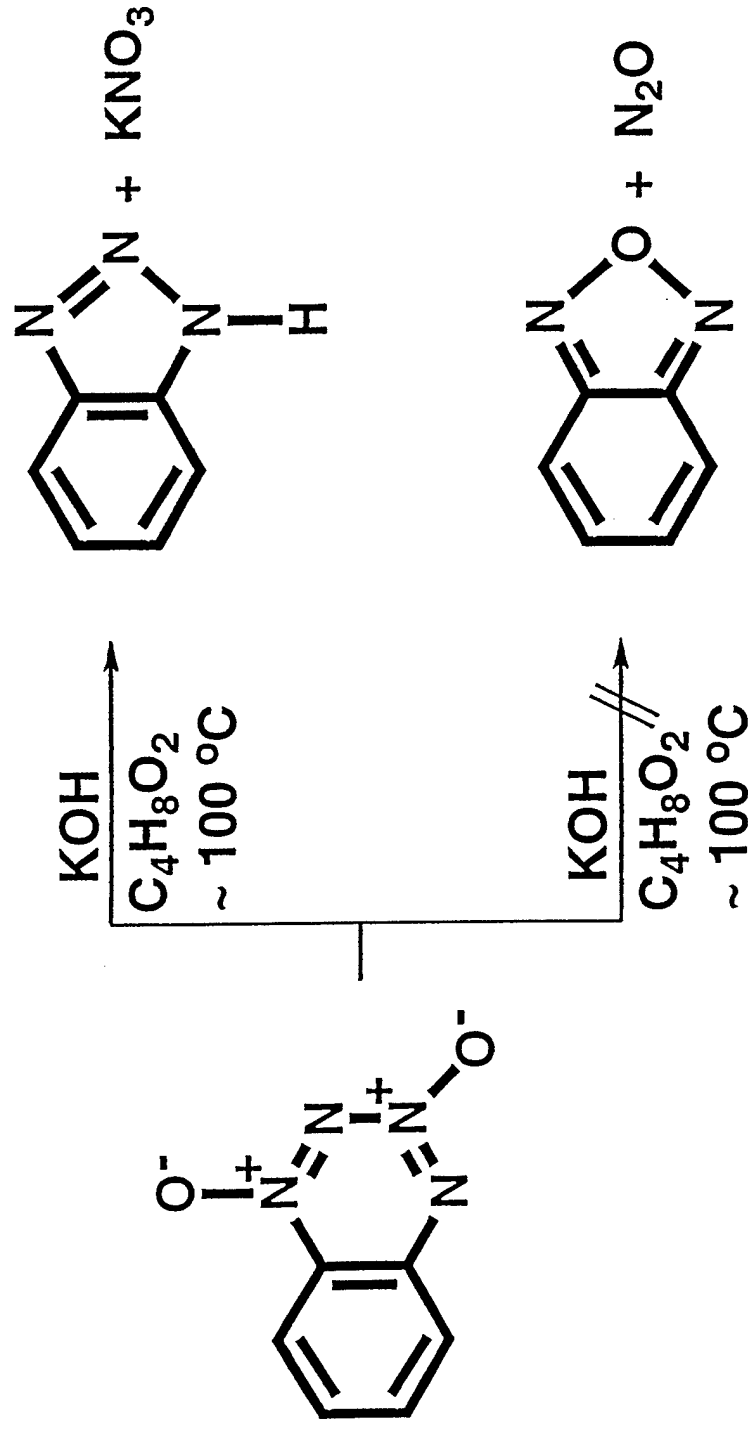


Syntheses of 1 and/or 2 are now being studied. Oxidations of 1 and 2 to quinone 3 or otherwise are to be investigated. Will the 1,2,3,4-tetrahydro-1,3-di-N-oxide ring system stay intact?



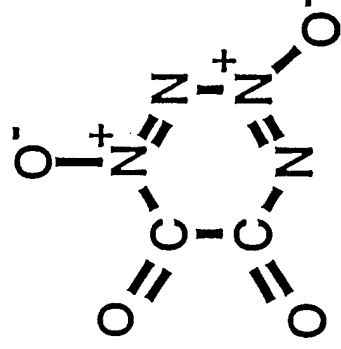
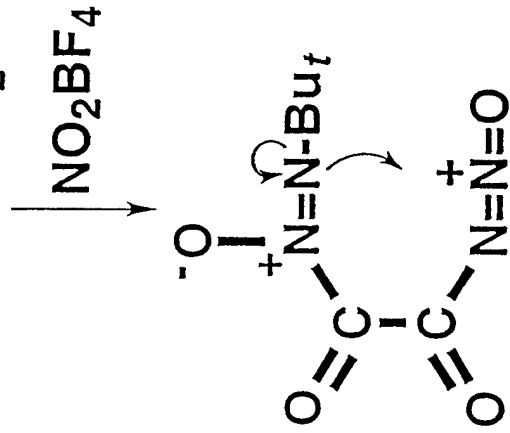
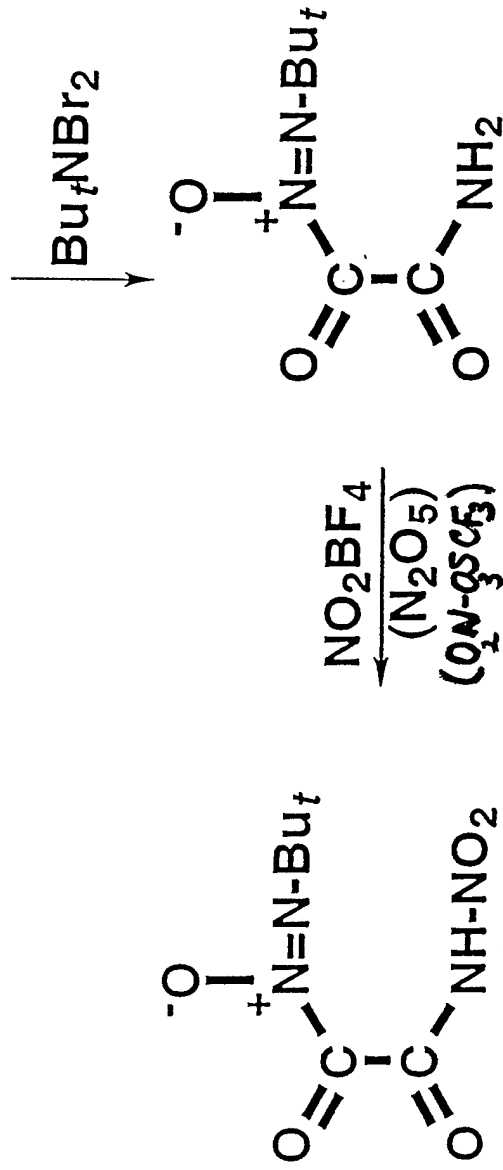
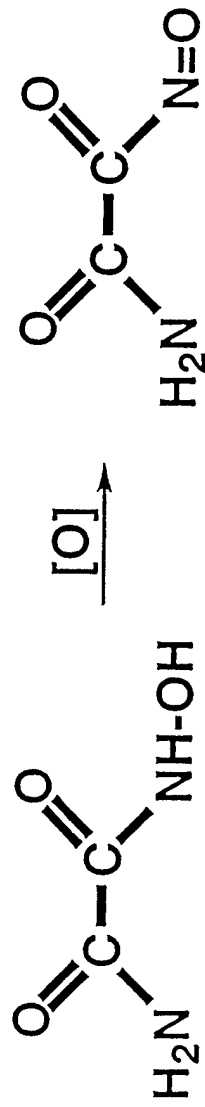


The low temperature behaviour of **1** with OH^- and with NH_2^- are being studied at OSU at present. The products indicated are to be oxidized in efforts to prepare 1,2,3,4-tetrazine-1,3-di-N-oxide derivatives, usable for preparation of DTTO and/or DSTTO.



Reaction of benzotriazole-1,3-di-N-oxide with hot KOH to give benzotriazole with expulsion of KNO_3 is unexpected. The effects of temperature on the above system are to be determined.

o-Quino-1,2,3,4-tetrazine 1,3-Dioxide (QTDO)

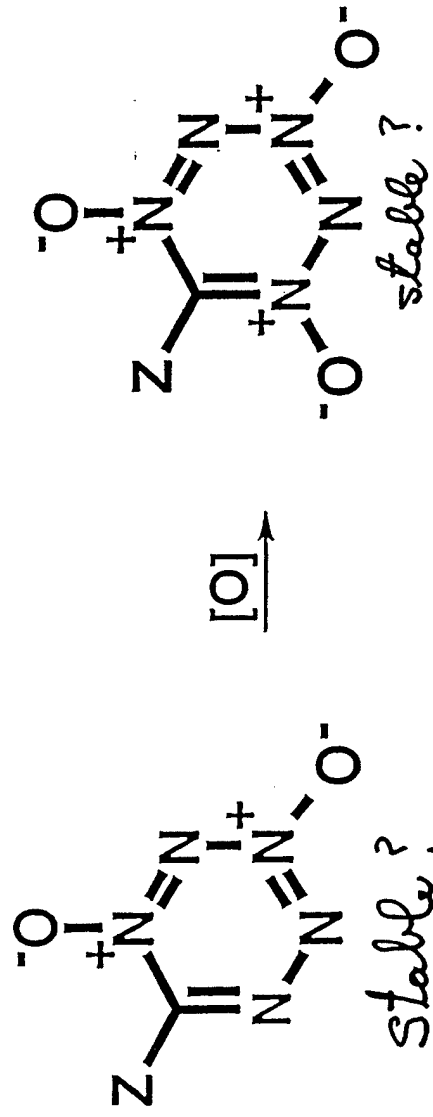
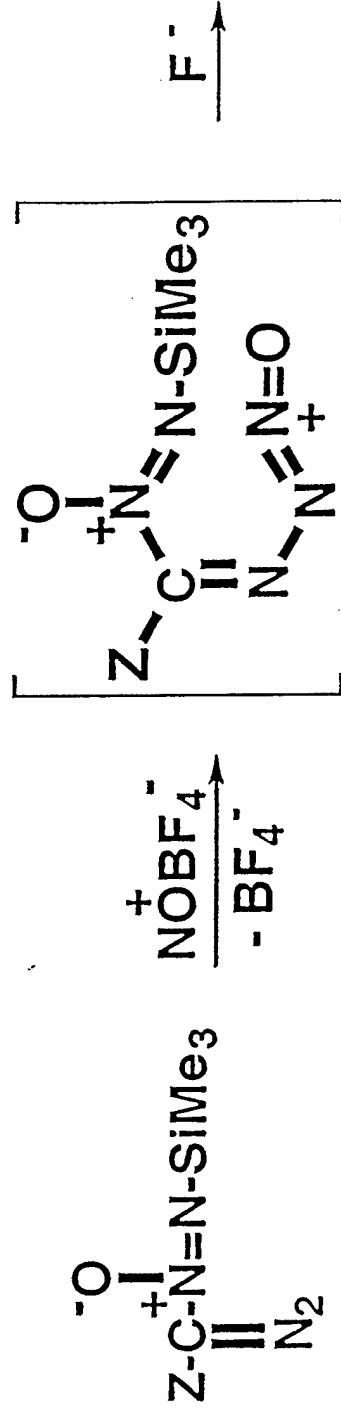


QTDO may be a cheap precursor to DTDO or an iso DTDO. Synthesis of QTDO as above has been proposed to DARPA/AirForce

QTDO is of interest as an energetic material and, in gasolines, etc, as a practical source of N_2O .

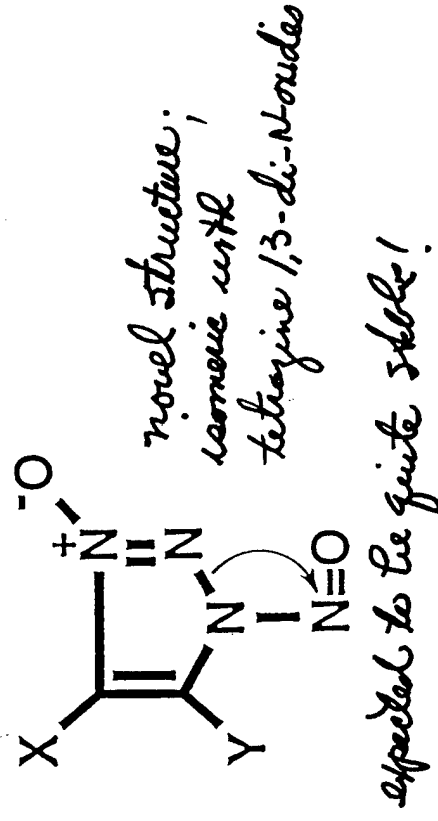
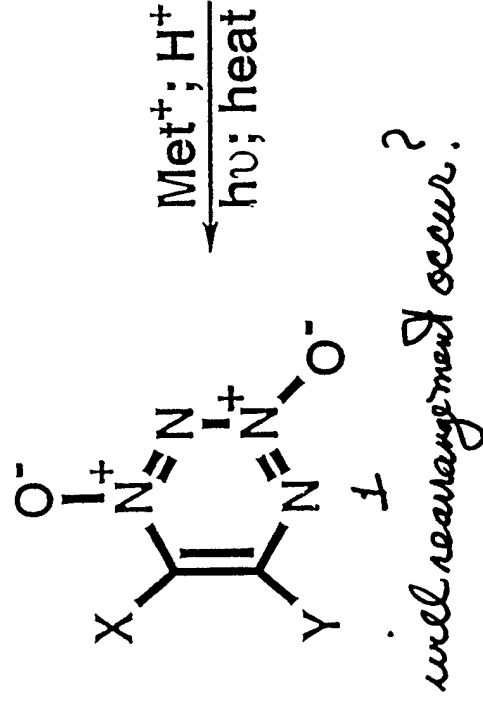
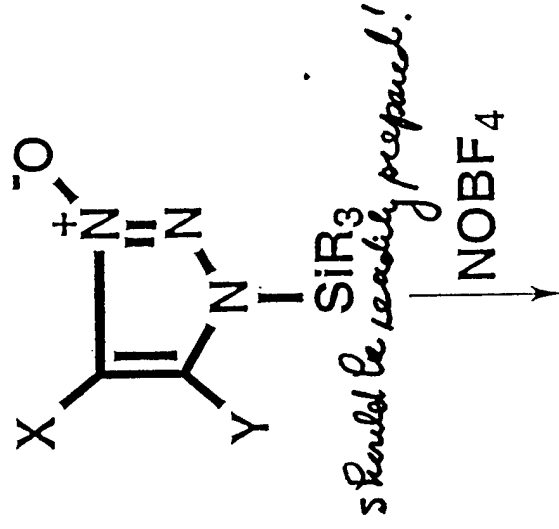
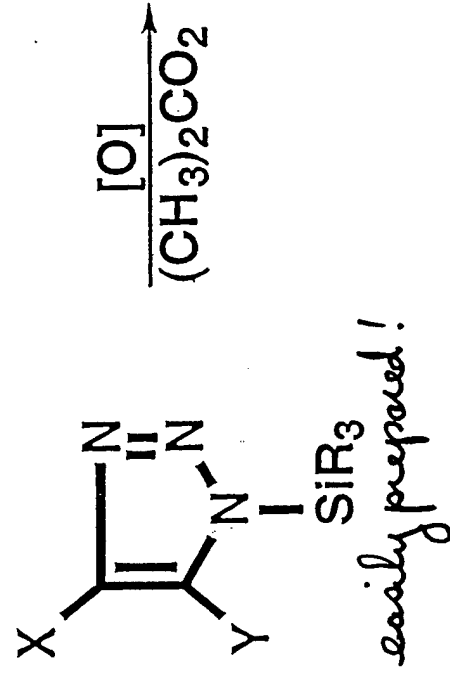
Possible Synthesis of Pentazine N-Oxides

Pentazine N-Oxides are unknown; α -diazides should be stable, highly interesting new structures; the following sequence involves new reaction schemes.



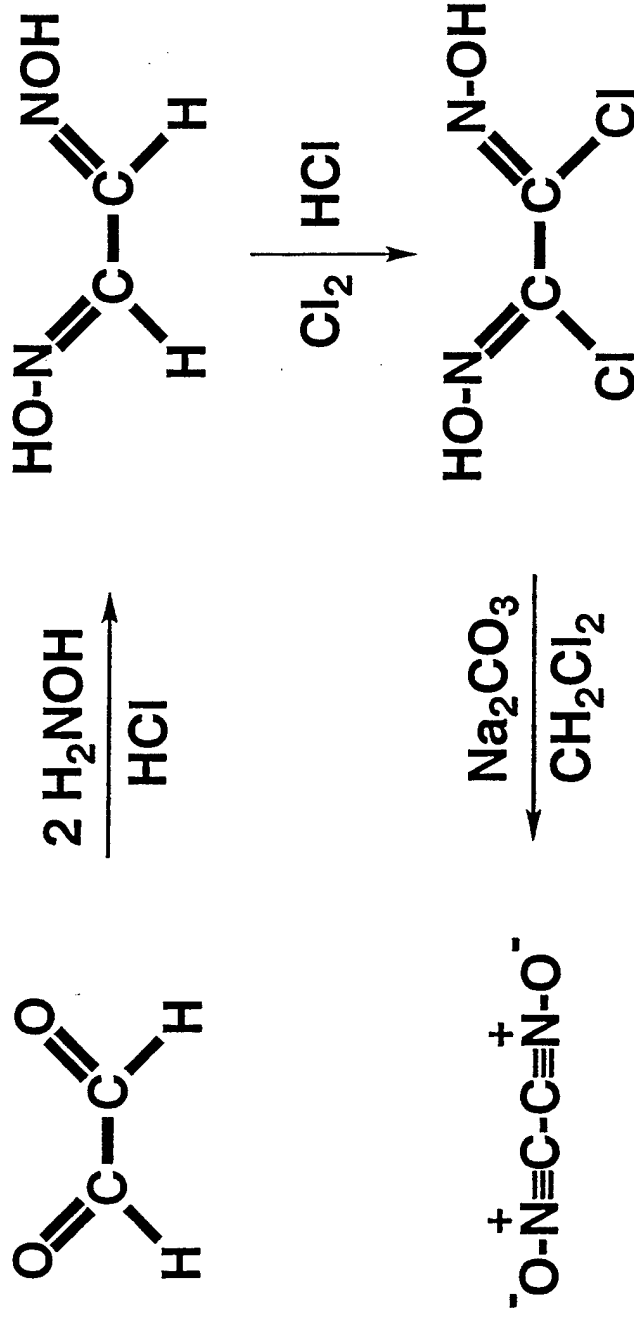
Z = H, R, Ar, NO₂, CN, RO, X, etc.

Proposed Synthesis of Tetrazine 1,3-Di-N-oxides



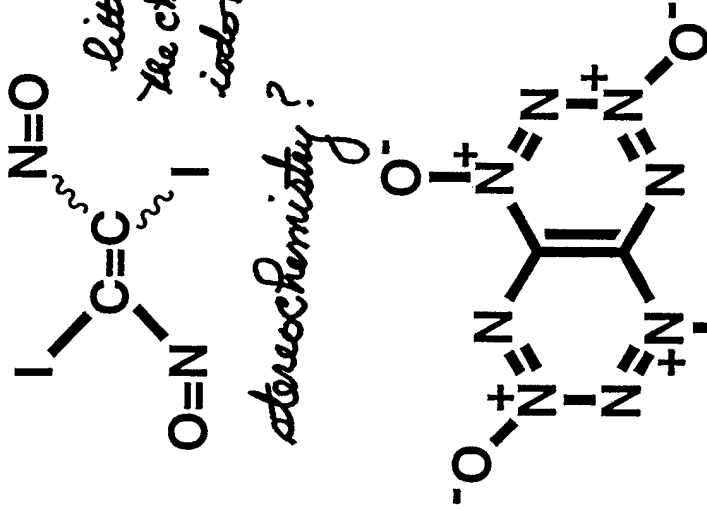
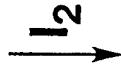
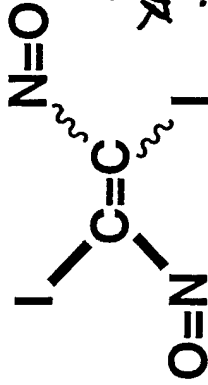
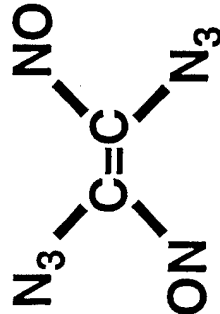
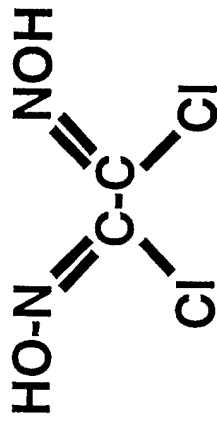
Vary X, Y, R₃Si and Oxidant

Synthesis of Cyanogen N,N'-dioxide



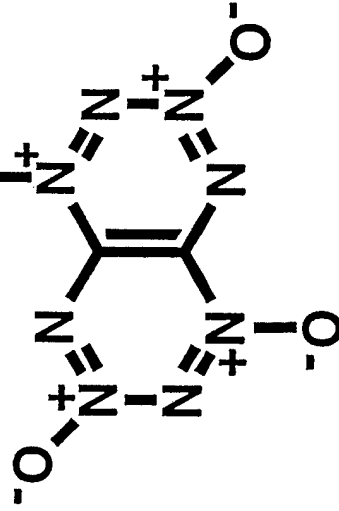
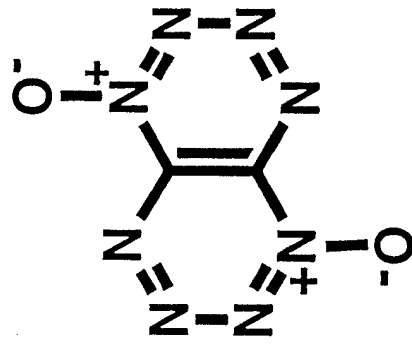
Major programs involving cyanogen N,N'-dioxide for synthesis of energetic materials may be envisaged.

Synthesis of IsoDITTO



stereochemistry?

little is known of the chemistry of cis-iodonitroso compounds!



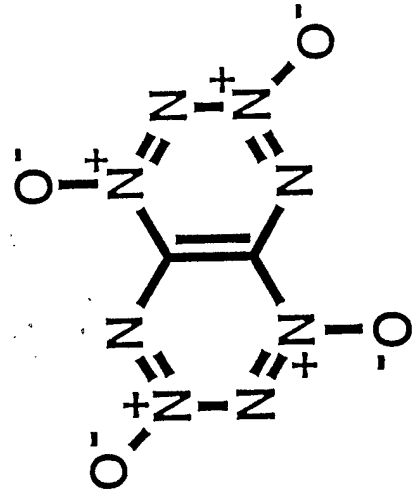
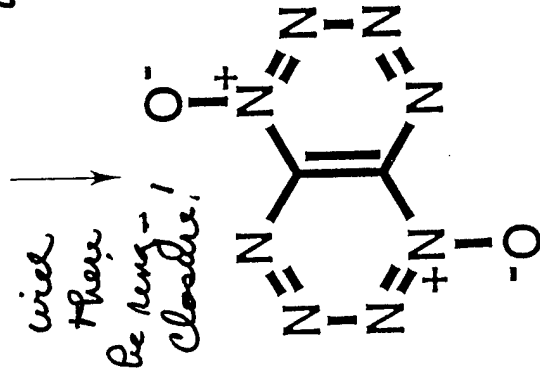
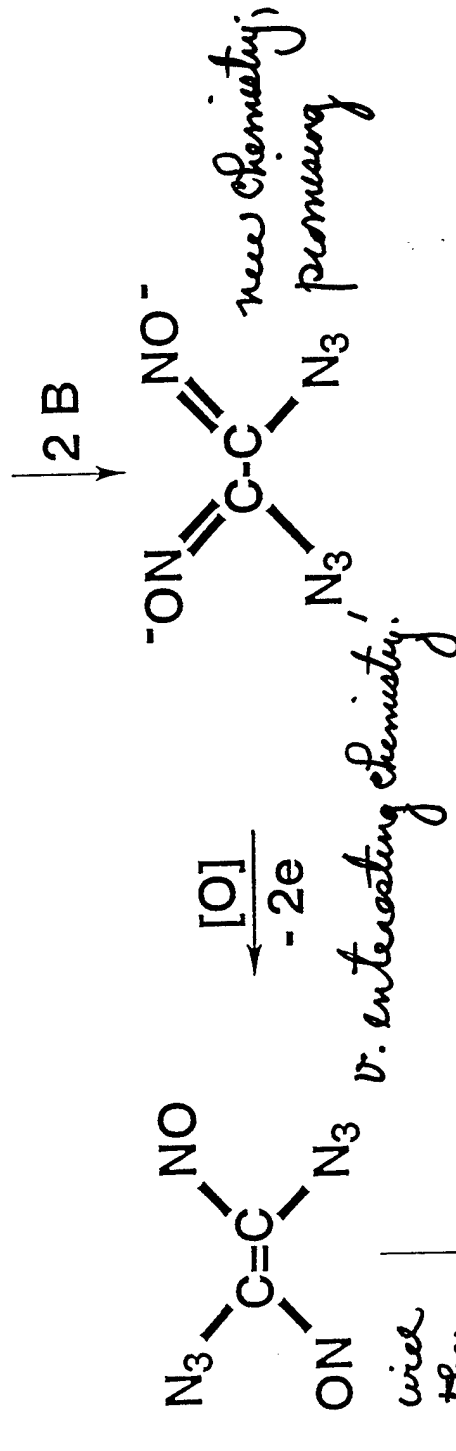
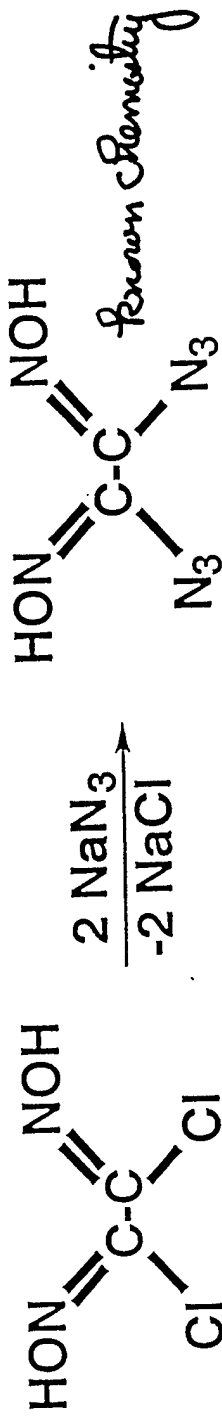
stability?

nothing is known of the behavior of cis-azidonitroso defns.

Do they cycl

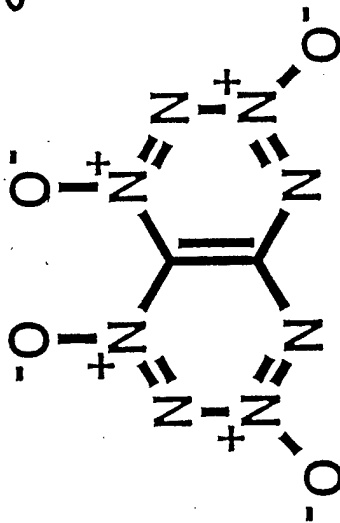
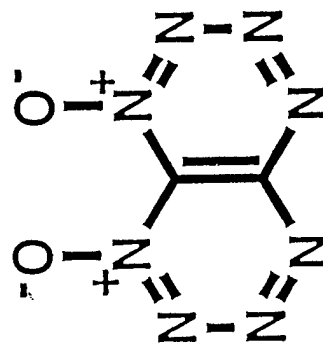
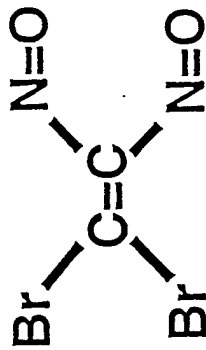
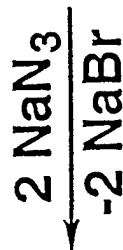
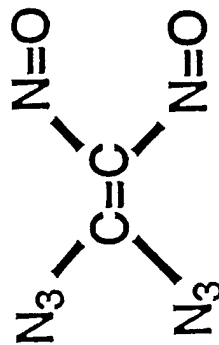
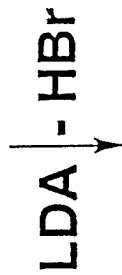
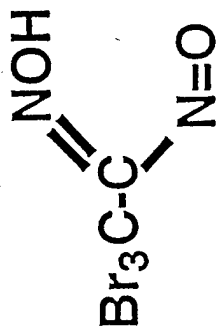
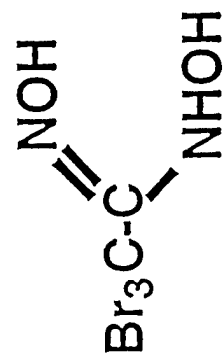
The oxidizing agent will have to be selective.

Possible Synthesis of IsoDTTO



This synthesis of IsoDTTO has not been investigated as yet.
Successful IsoDTTO will be inexpensive!

Possible Synthesis of DTTO

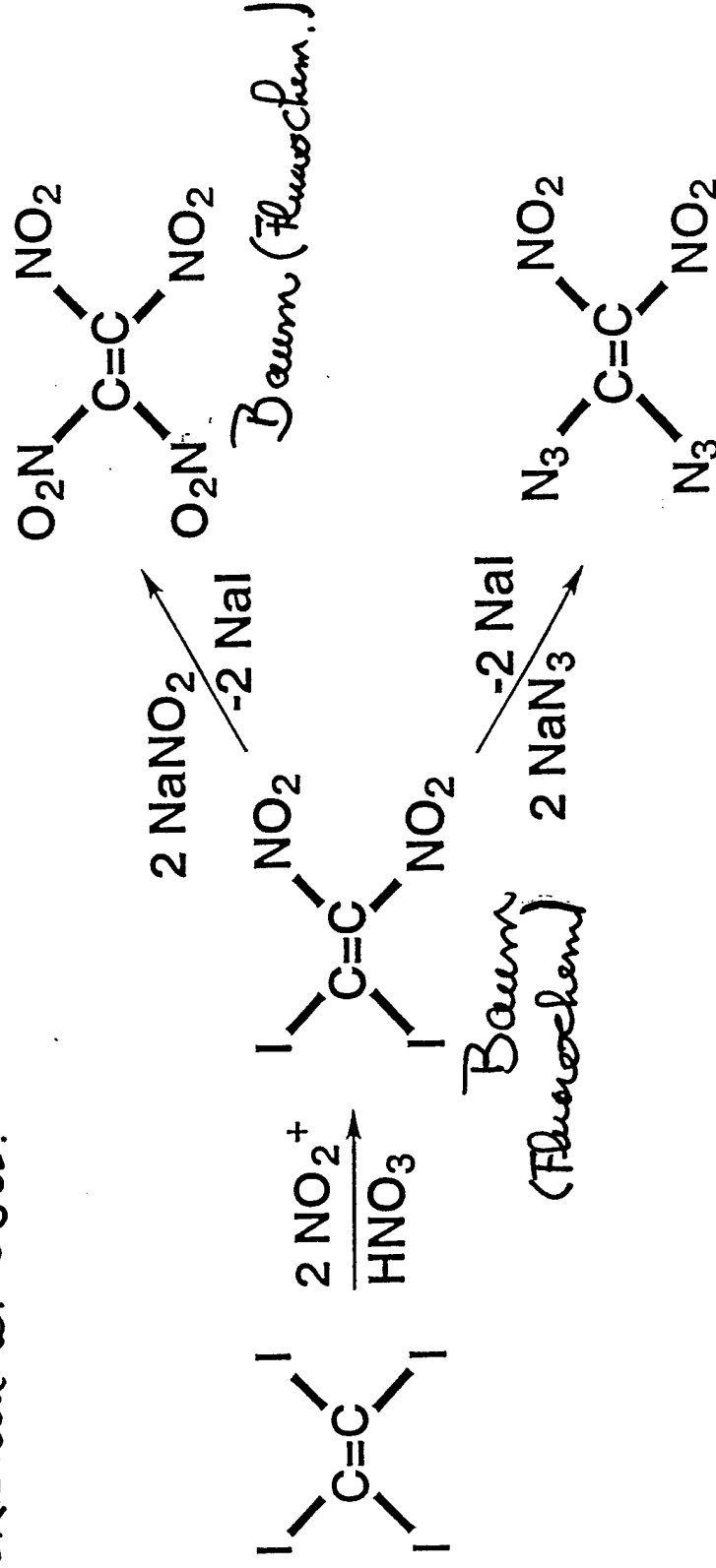


Again, do ris-
cydrazides
ring close to
tetrazine-mono-
N-oxides?

major problems
based on 1,1-dinitros
olefins and
tetranitrosoethylene
should be carefully
evaluated.



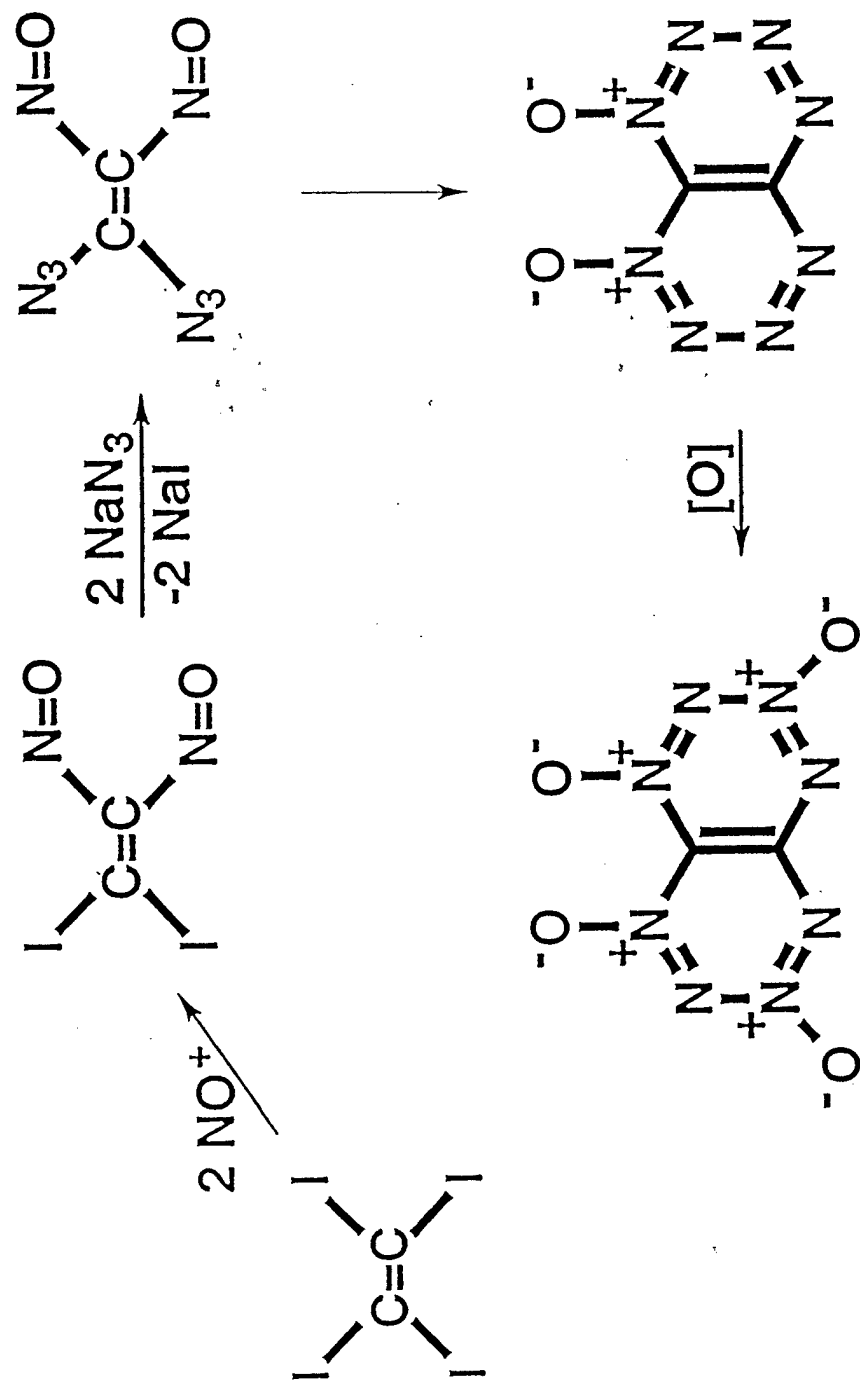
This sequence was developed by Baum at Fluorchem and by Alekseeva at OSU.



Alekseeva (OSU)
 A very interesting molecule
 prepared here which
 has not been studied
 further.

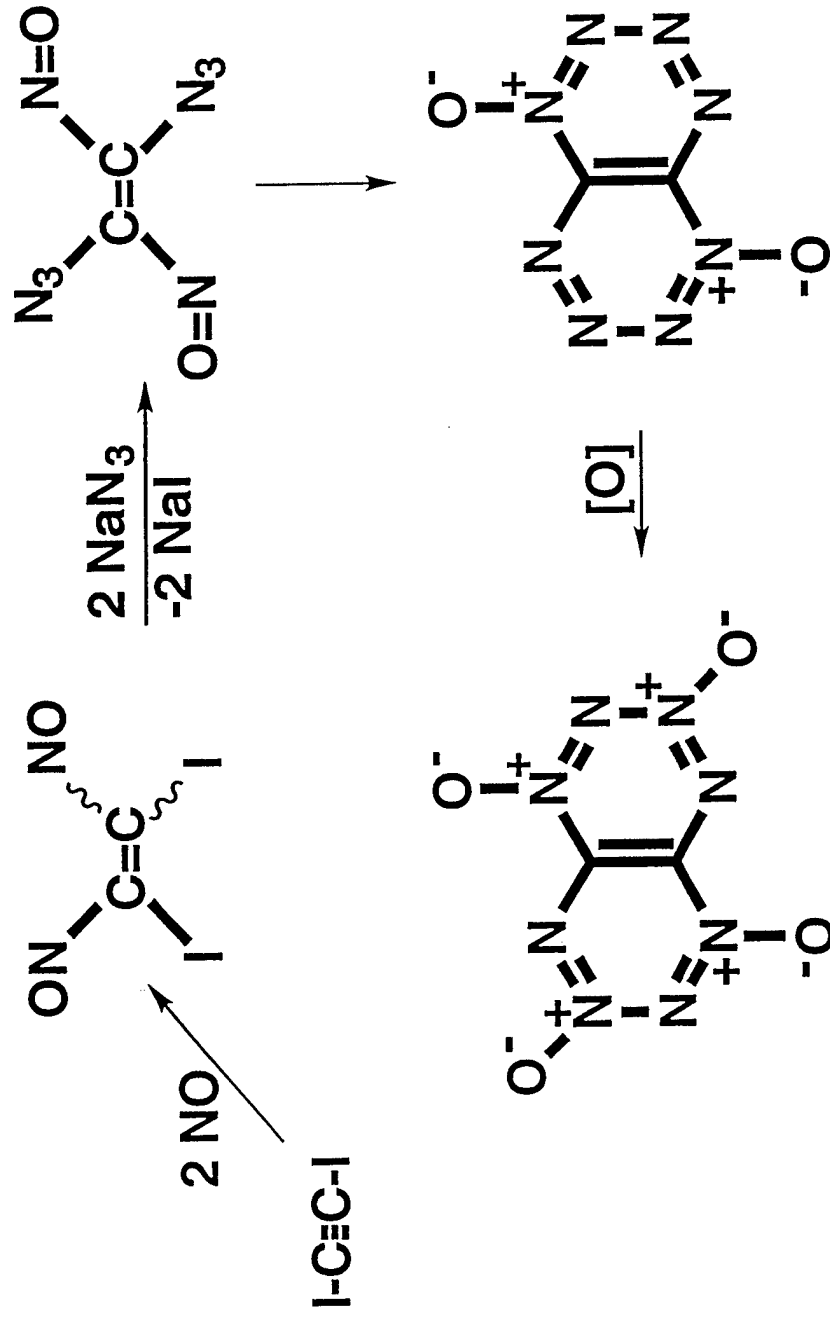
Baum; Alekseeva

Possible Synthesis of DTTO



Major problems on use of tetrachloroethylene, trichloroethylene, and dichloroethylene should be evaluated.

Possible Synthesis of IsoDTTO



Reactions of diiodoacetylene and N_2O_4 (and other nitroting agents) are being studied on a DARPA program at Ohio State.